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PHYSICO-CHEMICAL METHODS

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PHYSICO-CHEMICAL PRACTICAL EXERCISES
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PHYSICO-CHEMICAL METHODS

BY

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PREFACE

IN *Physico-Chemical Methods* an attempt has been made to provide an orderly presentation of those border-line practical problems of interest to both the chemist and physicist. More than two decades have passed since the text was first published, and during this period there have been many developments. The scope of experimental physical chemistry is wide, and the tendency is for the subject to subdivide into numerous highly specialized sections. With this expansion, to cover the subject, even in a general manner, is a formidable task. The authors have endeavoured to produce a connected work rather than a series of monographs on isolated, restricted topics. Under the circumstances, with the gradual growth, systematic classification is difficult and it may be necessary to regroup sections later under more connected headings.

In this supplementary volume, chapters on Atomic Weights, Mass Spectrography, and Electron Optics are included. Increased attention has been given to the study of molecular properties, e.g. Molecular Weights, Diffusion, Solution, Adsorption, Kinetics of Homogeneous Reactions, Colloids, &c. Other sections also have been expanded, e.g. Hydrogenation, Chromatography, Micro-gas Analysis, High-temperature Technique, Electrolytic Oxidation, &c.

The worker in Practical Physical Chemistry is fortunate in having a wide current literature to aid him, and such journals as those produced by the American and British Chemical and Physical Societies, with their Transactions and Abstracts, give a good starting-point in reading. Reference is made here to a few journals, but the authors' thanks are due to many, and, as far as possible, acknowledgements have been recorded throughout the text. *Industrial and Engineering Chemistry,* now under the sub-title of *Analytical Chemistry,* has been found specially helpful, and the authors wish to thank the Editor, Mr. Walter J. Murphy, for his co-operation. Dr. J. H. Lang, Editor of the *Journal of Scientific Instruments,* has also been helpful and has kindly provided a number of electros.

We are indebted to the late Dr. F. W. Aston, F.R.S., for advice on the chapter on the Mass Spectrograph and for valuable criticism of it in the manuscript form. The newer mass spectrometers which greatly facilitate certain types of analysis have received some consideration. Mr. G. Burrows, of Metropolitan Vickers, has written the chapters on Electrolytic Oxidation. The chapter on Colloids in the previous edition has been completely revised to include details of many problems in both colloids and emulsions. For this task we are greatly indebted to Dr. J. C. Aherne. Chromatography has also been revised and rewritten by Mr. J. Devlin. General help in the task of revising, proof reading, &c., has been obtained from Dr. Desmond Reilly, who is also responsible for the notes on Biochemical Applications.

Fellow-workers have again generously co-operated and we have received suggestions and reprints of papers from many sources. Without this valuable aid, our task would have been much more difficult.

J. R.
W. N. R.

June 1948

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CHAPTER I [3]

ELECTRON OPTICS

SECTION 1: THE ELECTRON MICROSCOPE

IN 1856 Abbe showed that the least distance capable of resolution by an optical microscope was governed by the nature of the objective lens and was given by $\lambda/\mathrm{N}\sin\alpha$, where λ is the wave-length of the light used, N is the refractive index of the glass of the lens and α is the semi-vertical angle of the cone of rays entering the lens. To get high resolution it is necessary to use a short wave-length for the light and a large numerical aperture ($\mathrm{N}\sin\alpha$). The best oil immersion microscope can resolve to 10^{-5} cm.

In 1938 Kohler used ultra-violet light of wave-length 2,100 Å and a quartz optical system and was able to obtain resolution to 8×10^{-6} cm. Further progress in this direction is unlikely. In 1924 de Broglie showed that a particle of mass m and moving with a velocity v should have associated with it a wave-length λ given by $\lambda = h/mv$ where h is Planck's quantum. Shortly afterwards this was demonstrated experimentally by G. P. Thomson and others. The cathode ray tube gives just such a source of rapidly moving particles. Here the velocity of the electrons is determined by the potential difference across the tube and is given by $v = \sqrt{\frac{2\,e\mathrm{V}}{m}}$ where e is the charge on the electron and V the potential difference. Hence

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2me\mathrm{V}}} = \frac{k}{\sqrt{\mathrm{V}}}$$

so with an applied P.D. of 60 kv. the wave-length works out to the order of 0·1 Å, about 50,000 times shorter than the wave-length in the middle of the visible spectrum.

Busch, 1926, discovered that an axially symmetrical magnetic field caused an electron travelling in the direction of the field to take a spiral path, and if a magnetic field of limited extent was used it led to the beam of electrons being brought to a focus.

The first electron microscope to be designed on these principles was made by Knoll and Ruska.[1] The instrument was of the projection type and employed electromagnetic focusing in two stages. The magnetic field was limited by enclosing the coils in iron shields. The magnification obtained with this instrument was not so good as that obtainable with the optical microscope. v. Borries and Ruska [2] have improved the instrument so that resolution to 3×10^{-7} cm. is possible.

[1] *Z. Phys.*, 1932, *78*, 318.

[2] *Z. tech. Phys.*, 1939, *20*, 225.

The electron beam from the discharge tube is accelerated to 60 kv. and is condensed by the first electromagnetic coil on to the object which is mounted directly in front of the second electromagnetic coil which acts as the objective and forms an intermediate image directly in front of the third or projector electromagnetic coil which produces the final image projected on to a fluorescent screen or a photographic plate : focusing is carried out by varying the current in the coils of the electro-magnets. The instrument is about 150 cm. high and is mounted on a heavy base which stands on the ground, the screen being viewed through a window looking downwards at a height of about 100 cm. from the ground. A high vacuum must be maintained in the lens system in order to prevent absorption or scattering of electrons so that it is necessary to provide air locks for the introduction of the object and the photographic plate so as to reduce the subsequent pumping to a minimum. The object to be examined is mounted on a very thin strip of celluloid. Because of the high vacuum solid objects are more suitable for examination than biological preparations. Special methods are devised for particular cases ; thus metal surfaces have been examined by coating the surface with a layer of resin which is afterwards peeled off and examined. The photographs obtained with the instrument are sometimes fit for further enlargement up to 5 diameters.

Since the continued impact of the electrons on the object being viewed might cause considerable damage, the electron beam is deflected away from the object by a subsidiary coil while adjustments are being carried out, since it takes some time for the beam to settle down to a steady state and it is then undesirable to interrupt it. This instability of the discharge tube is an important defect of the electromagnetic form of apparatus and causes streaking of the image. It does not affect the electrostatic system of focusing. Instruments of this type are now available.

Electrostatic Focusing

When an electron passes across a plane interface between a field of potential V to one of potential V^1, it is refracted in such a way that

$$\sqrt{V}.\sin\theta = \sqrt{V^1}.\sin\theta^1$$

where θ and θ^1 are respectively angles of incidence and refraction.

If the interface between the two fields is a part of a sphere of radius r, there exists a conjugate relationship between the distances of the object and image, u and v respectively, and the radius of curvature r, completely analogous to the optical case. The relation is

$$\frac{\sqrt{V^1}}{v} - \frac{\sqrt{V}}{u} = \frac{\sqrt{V^1} - \sqrt{V}}{r}$$

The field of potential V^1 may be limited in size and shape in such a way as to form an equi-curved electrostatic lens, behaving towards a beam of electrons exactly as a convex lens does in the case of a beam of light.

Brüche and Haagen [1], and Mahl [2] used lenses of this type having a central diaphragm at cathode potential and two outer diaphragms at zero potential. A focusing electrostatic field of more or less restricted extent is set up in and around the central apertures of the diaphragms. This type of electron optical system has the advantage over electromagnetic focusing in that when the lens potential is the same as that of the cathode potential stabilization of the latter is unnecessary. The resolution obtained was 2×10^{-6} cm.

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[1] *Naturwiss.*, 1939, *27*, 809.

[2] *Z. tech. Phys.*, 1939, *20*, 316.

Spherical aberration similar to that which occurs in optical lenses is a defect of both the electrostatic and the electromagnetic system and causes a large error even for lenses of small aperture.

Electron Shadow Microscopes were described by Morton and Romberg[1] and Boersch[2] in which the electron source is made very small so as to conform as nearly as possible to a point source. The object to be examined is brought as near as possible to the source and a shadow picture is thrown on a fluorescent screen or photographic plate some distance away. The magnification is the ratio of the distance of the screen from the source to that of the object from the source. A resolution of 4×10^{-6} cm. was obtained. There is no question of refraction in this instrument.

A new principle was introduced by v. Ardenne[3] in the scanning electron microscope. The cathode of the discharge tube emits a beam of electrons which is focused to a 'crossover' of minute cross-sectional area. This cross-section is still further reduced by electrostatic 'demagnifying' lenses until it is only 10^{-12} cm. This fine point of electrons then impinges on the object over which it is moved by a scanning magnetic field of the type used in television. The electron beam as transmitted through the object is amplified and applied to the modulator of a television tube and the magnified image projected on to a fluorescent screen. The resolution obtained is only 10^{-5} cm.

The analogy to the ordinary light microscope is seen in Fig. 1 (I^3) and Fig. 2 (I^3). In the light microscope the light from the source first passes through the condenser which concentrates it on the object which is thereby very brightly illuminated. The light then passes through the objective system to produce the first image. When an eyepiece is used this produces a second magnified and virtual image but if the eyepiece is replaced by a camera the projector lens of this gives a second magnified and real image on the ground glass screen used for focusing and so on the photographic plate. Each of these steps is closely followed in the electron microscope of which a simplified diagram is given in Fig. 3 (I^3). Not only is there this similarity in the first order properties of optical and electron microscopes but also in their defects. All types of aberrations found in glass lenses find their counterparts in electron optics. The Radio Corporation of America has developed in a commercial form the R.C.A. Electron Microscope and a considerable number of these are now in use.[4] In the R.C.A. instrument the electron gun assembly contains a 'V'-shaped tungsten filament which is heated by the output of an R.F. oscillator. The electron accelerating voltage is produced by placing the cathode at a potential of 30 to 60 kilovolts below that of the anode which is earthed. The electromagnetic condenser lens, which prevents the scattering of the beam of electrons and concentrates it on the object, consists of a coil form containing a large number of turns of wire through which the condenser current flows. This current produces a magnetic field which bends the electron beam just as an optical lens bends a light beam. Varying the condenser current varies the field strength and thus produces a change in the focal length of the magnetic condenser lens. The objective lens of the electron microscope, like the objective of a light microscope, produces an image of an object which is placed between it and the condenser lens. It is possible to view this image on a fluorescent screen, when a magnification of about 100 diameters is obtained. The electromagnetic projector coil or lens then magnifies a small portion of this image and produces a final image on a fluorescent screen usually coated with Willemite. The projector lens produces additional magnification up to 250 times, thus permitting the instrument to provide a direct magnification of 25,000 diameters.

---

[1] *Phys. Rev.*, 1939, *56*, 705.

[2] *Z. tech. Phys.*, 1939, *20*, 346.

[3] *Ibid.*, 1939, *20*, 239.

[4] We are in debt to Mr. W. J. Reilly of the R.C.A. Manufacturing Co., Camden, N.J., for Figs. 1, 2, and 3.

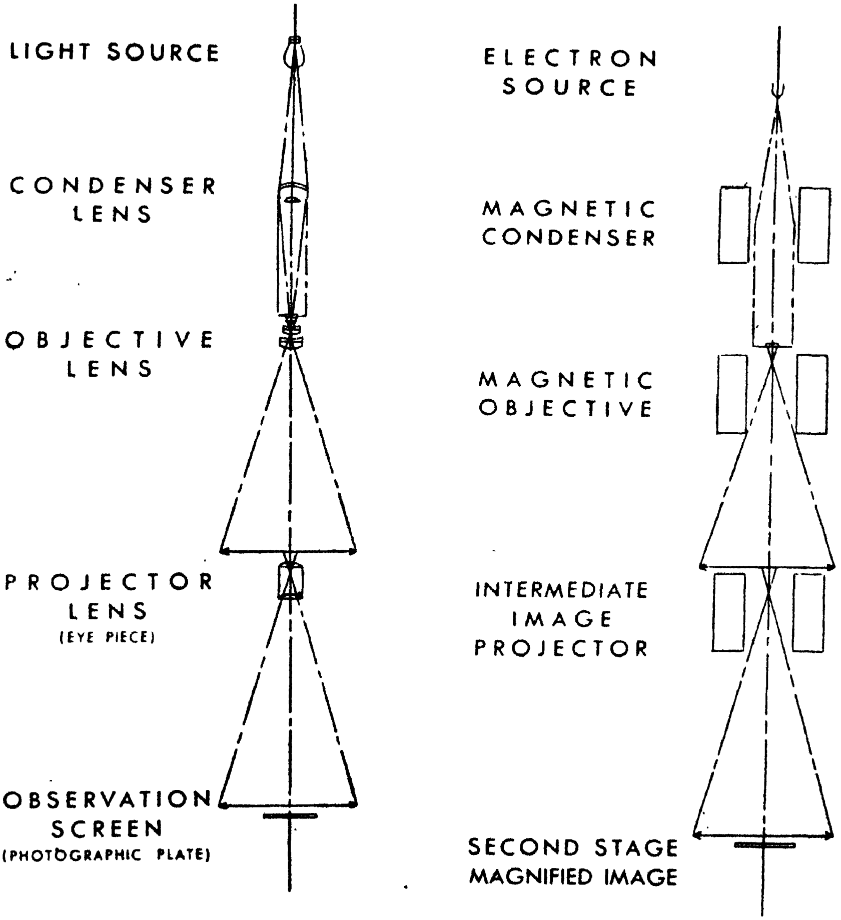
LIGHT SOURCE
CONDENSER LENS
OBJECTIVE LENS
PROJECTOR LENS (EYE PIECE)
OBSERVATION SCREEN (PHOTOGRAPHIC PLATE)
ELECTRON SOURCE
MAGNETIC CONDENSER
MAGNETIC OBJECTIVE
INTERMEDIATE IMAGE PROJECTOR
SECOND STAGE MAGNIFIED IMAGE

FIG. 1 (I[3]) FIG. 2 (I[3])

Analogy between light microscope and electron microscope

The final viewing screen can be raised with a simple mechanism exposing a photographic plate to the electron beam. Thus it is possible to obtain a permanent record of the greatly enlarged image of the specimen or object. It is found that, due to the excellent resolution of the electron microscope,

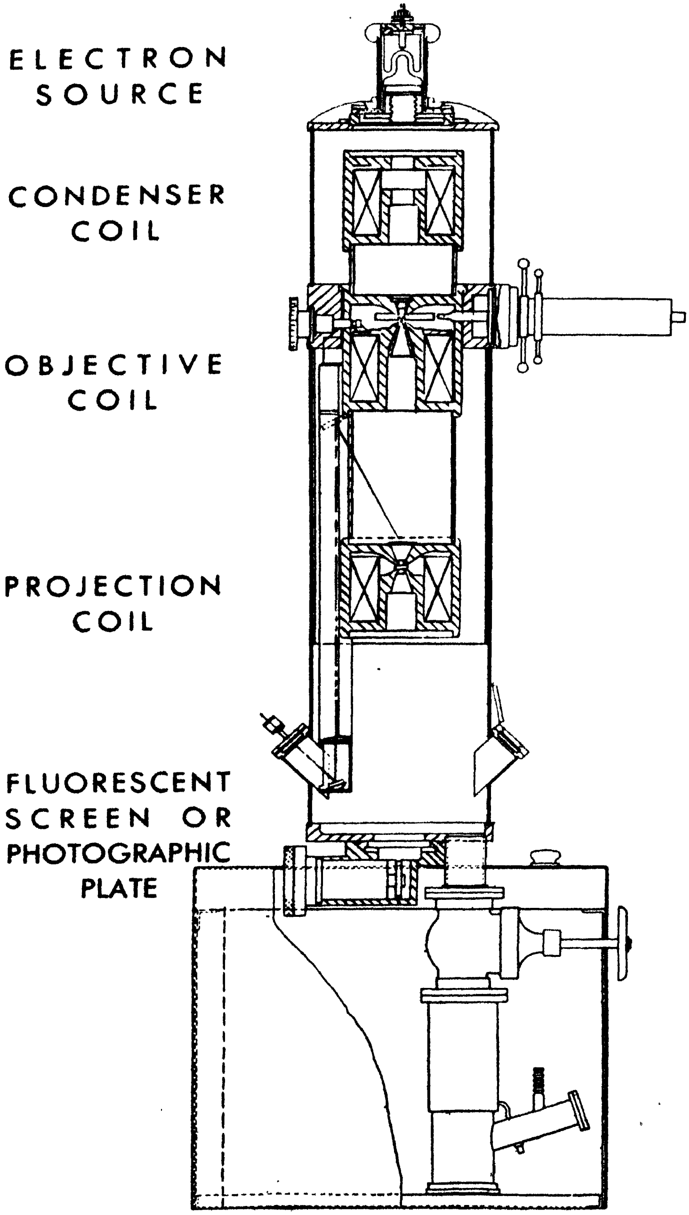

FIG. 3 (I')
Electron microscope

it is possible to obtain photographically a further magnification of about four times.

Varying the objective coil current, which can be accomplished by means of a coarse, a fine and finally a vernier control, results in a change of focus. Changing the projector coil current effects a change in magnification. This can be accomplished in a series of steps. Furthermore, by mounting the specimens in either the bottom or top of the specimen holder a great range of magnification can be obtained. In the former position from 3,500 to 25,000 and in the latter from 1,000 to 3,500. There are, therefore, now no gaps in the range of the light microscope and the highest magnification of the electron instrument.

Two of the difficulties which retarded the development of the electron microscope were—first, the necessity of a fairly high degree of vacuum in the microscope column and, secondly, the importance of an extremely well-regulated power supply. Both have now been overcome. It is sufficiently well known that a high vacuum is necessary when electrons are to be moved in the space between two electrodes. The column of the microscope is thus like a very large vacuum tube. Two mechanical megavac pumps and an oil diffusion pump are used to obtain a vacuum which is, of necessity, better than 10^{-4} mm. of mercury. The design of a system such as this capable of maintaining this degree of vacuum is sufficiently remarkable in view of the fact that there are several mechanical joints in the column to permit disassembly for transportation, cleaning, &c. One of the mechanical pumps acts as a backing pump for the oil diffusion pump and this is the principal means for evacuating the column. In order to concentrate the magnetic field at the very centre of the coils where they will have the greatest control over the beam, it is necessary to incorporate pole-pieces in the objective and projector coils and these pole-pieces contain comparatively small apertures. In order to reduce the pumping time, which would be considerable due to these apertures, a manifold or auxiliary column is built in and is connected with various points in the column and so facilitates the evacuation of those spaces which are separated by the small apertures.

The second or auxiliary mechanical pump is provided in conjunction with this auxiliary system. As it requires approximately ten minutes to evacuate the entire column, it is evident that this time factor would be objectionable when changing specimens or photographic plates. Consequently chambers are provided for the specimens and for photographic plates so that they can be sealed off from the remainder of the column, thus permitting a change of specimen or photographic plate with a resultant loss of vacuum in a comparatively small volume. Metallic bellows are employed in this connexion and also in various other places where mechanical movement is required in places where vacuum must be maintained. About one minute is required to evacuate the specimen or object chamber including pre-pumping time. After changing specimens or photographic plates, the chambers are pre-pumped, for partial evacuation, with the auxiliary mechanical pump and manifold system.

The taking of photographs with the electron microscope is a very simple procedure. The specimen can be scanned by turning specimen movement screws which move the specimen stage in which the specimen is mounted. This movement must be very precise, since it will be magnified in the image perhaps 25,000 times. A mechanical shutter is provided which permits limiting the field of view when taking pictures. The standard photographic plate is inserted in the casette which is light-tight and which is placed in the photographic chamber. This casette can be moved to the right or to the left with a casette movement control and the picture width is determined by this control. Exposure time is dependent simply on the time that the final viewing screen is maintained in an elevated position, as explained above.

The degree of vacuum may be checked by a thermocouple gauge circuit and by an ionization gauge circuit. The former provides only a rough check but one which suffices in most instances. Occasionally, however, when it is desired to obtain a more accurate measurement of vacuum the ionization gauge is used. The circuits are fairly simple and the degree of vacuum is proportional to currents which are measured by meters located on the control panel.

Exposures normally vary between ten seconds and two minutes. For very sharp pictures it is essential that the electron beam remains perfectly motionless. Any variations in high voltage or in coil currents will result in image movement or variation. It is for this reason that the R.C.A. Electron Microscope is designed so that the high voltage does not vary more than one part in 50,000. The stability of the condenser coil voltage supply must be better than 0·1 per cent, that of the objective voltage better than 0·0075 per cent and that of the projector coil better than 0·068 per cent. Separate regulated power supplies are provided for each of the magnetic lenses as well as for other purposes. As high operating voltages are used, safety interlock switches are built in and other safety precautions taken. The diagrammatic section shows that corona shields and rings are mounted on and above the electron gun to prevent high voltage arc-over.

As the various parts of the column are demountable, it is essential that a means be available for aligning each part in such a way that the electron beam will not be impeded in travelling through the tiny apertures which lie in its path. Alignment screws are provided and it is possible to move component parts of the column independently, again by the employment of metallic bellows. As an aid to alignment and in obtaining maximum image intensity, a provision is made for raising or lowering the filament. Furthermore, a window peephole makes it possible to view another fluorescent screen which is mounted directly above the condenser coil and which, of course, contains a hole for the passage of the electron beam.

The design for the three coils, particularly that of the objective and projector coils, is extremely important and critical when it is desired to obtain high magnification, high resolution, low distortion characteristics, and short focal length. The pole-pieces, in particular, require very careful design for the best results.

The fact that a sharp and excellent picture can be obtained on a photographic plate by exposing this to an electron beam that was focused on a fluorescent screen above the plate shows that this instrument has great depth of focus. This is well shown in pictures of crystals where different crystal planes all appear in sharp focus. The depth of focus is actually better than 10 microns.

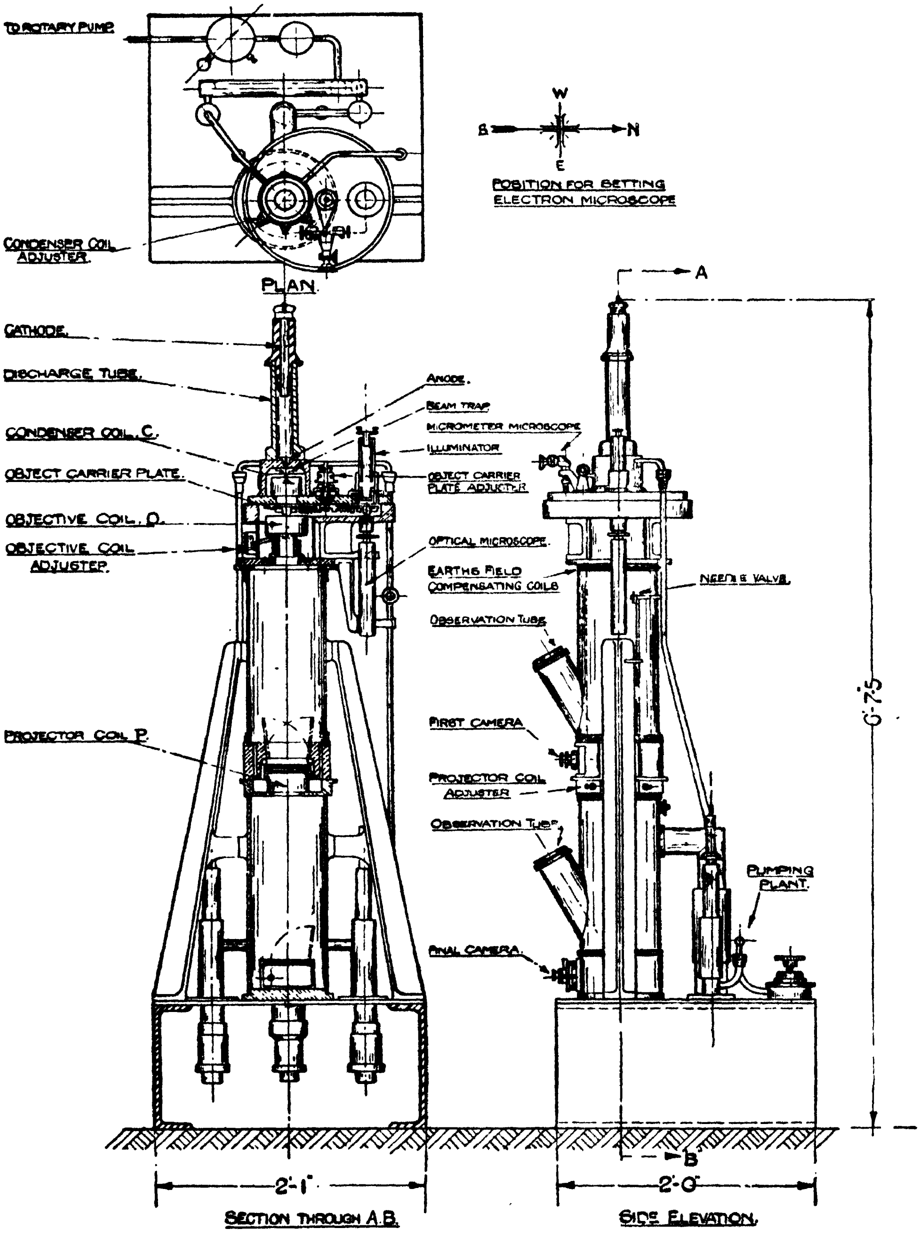

FIG. 4 (I^3)
Electron microscope mounted on base-plate

The controls on the panel include, in addition to the vacuum indicator meters, controls for varying the current in each of the three coils, a control for varying the high voltage from 30 to 60 kilovolts in 5-kilovolt steps, a control for varying the beam current and a beam current indicating meter, a test meter and switch for making test readings of voltages and currents in various circuits, a relay indicator (an overload relay is provided in the circuit and a neon bulb flashes when the relay opens), a button for resetting the relay, and various switches for controlling panel lighting and power in the various circuits.

Metropolitan-Vickers, in 1935, in conjunction with Professor L. C. Martin, designed an electron microscope for the Imperial College of Science.[1] The body of the instrument consists of a vacuum-tight brass cylinder, divided into two portions, upon the upper of which is located the vacuum housing for the object-holder. Above this is located the housing for the condenser coil, and this housing in turn supports the discharge tube, which is of the type developed by Burch and Whelpton for use in connexion with the high-speed cathode-ray oscillograph.

The main tube contains the objective coil, intermediate camera, objective coil and final camera. Inclined observation tubes are provided for visual observation of the intermediate and final images. Evacuation is effected by two metrovac oil condensation pumps in series, backed by a D.R.I. rotary pump ; this system is found to maintain a high vacuum, despite the leakage of air through the anode hole from the discharge tube, where the maintenance of the discharge requires a pressure of from 0·01 to 0·1 mm. of mercury. The whole instrument, shown (Fig. 4 (I^3)), is mounted on a heavy base-plate resting on a concrete block in the floor of the laboratory ; the rotary pumps are mounted separately, and connected to the pumping system by rubber pipes to avoid communicated vibration.

Object-Holder. The use of magnifications of such a high order makes a preliminary optical examination of the object necessary. The whole field of the object is first examined by means of an optical microscope and particular sections of this field can then be selected for observation by the electron-microscope. The optical microscope cannot be mounted on the axis of the electron beam ; the instrument is therefore provided with a large disk which can be rotated, without breaking the vacuum, about an axis offset from the axis of the electron beam ; this assembly is shown by the section in Fig. 5 (I^3). The disk is fitted with two radial slides at 180° to each other, each carrying an object-holder, which may be given a radial movement by means of a fine external adjustment. The position of the object-holder may thus be adjusted in two directions at right angles, the circumferential movement being measured on a divided circle through a low-power microscope. Early laboratory tests at low magnifications were greatly facilitated by the use of these adjustments which made possible direct comparison of electron and visual images.[2]

The object-holders proper take the form of a heavy hollow copper zone, having a hole 0·008 inch diameter at the extremity. The object is placed on a thin film of metal or organic material in this hole. The heat generated in the object is thus readily removed by conduction.

---

[1] Our thanks are due to Metropolitan-Vickers Electrical Company and to Mr. G. Burrows for information on this firm's instruments and to the Editor of the *Journal of Scientific Instruments* for Figs. 4 (I^3) and 5 (I^3).

[2] *Metropolitan-Vickers Gazette,* Leaflet, No. 902/3—1 by Nuttall.

Magnetic Lenses. Two of these are seen in the previous figure and they are designed to produce a symmetrical magnetic field between two small annular pole-pieces concentric with the axis of the beam. The coils, which are wound in three sections, are contained in soft iron shrouds, into which can be screwed the pole-pieces, separated by a brass ring. Each coil section is separated from the next by a brass spacer, the function of which is to assist in the carrying away of heat from the windings. Although, from the point of view of good vacuum technique, it would have been desirable to use enamelled wire, it was found impossible by this means to obtain

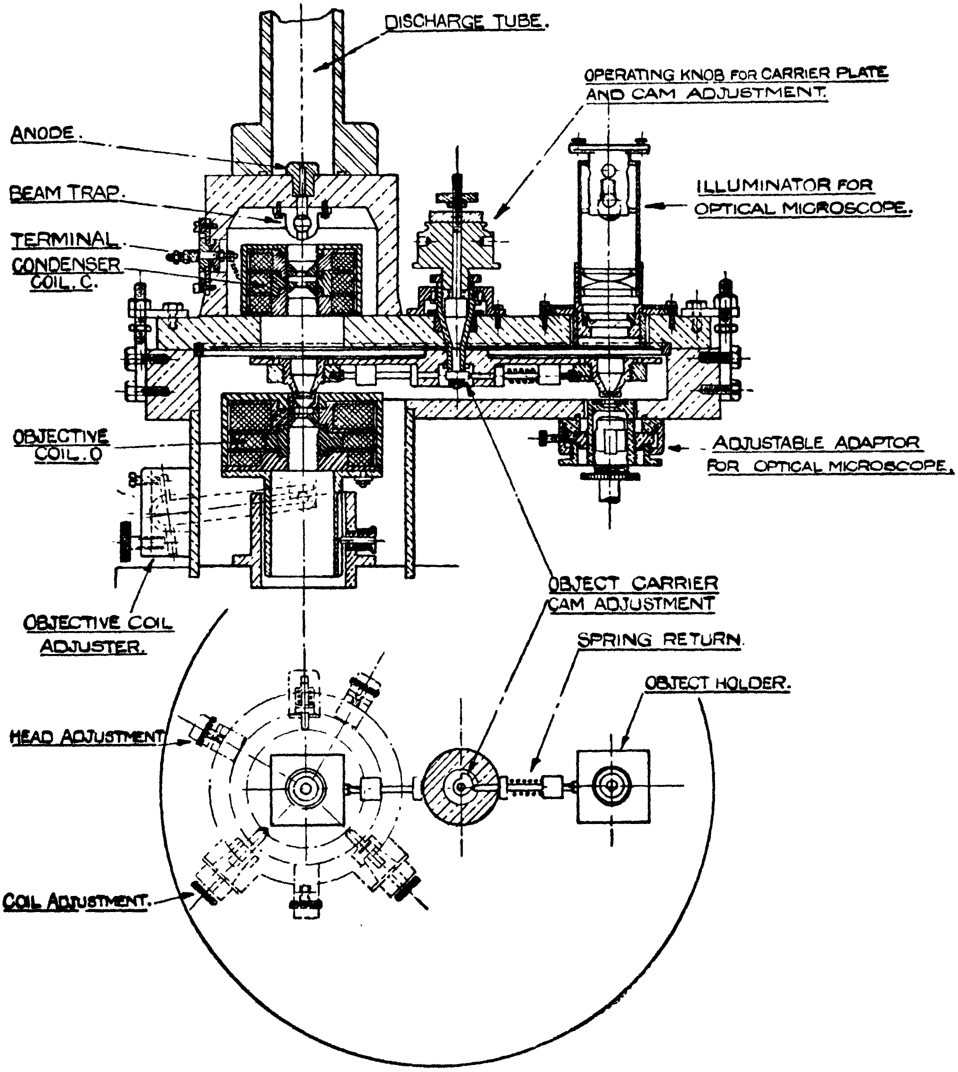
DISCHARGE TUBE.
OPERATING KNOB FOR CARRIER PLATE AND CAM ADJUSTMENT.
ANODE.
BEAM TRAP.
ILLUMINATOR FOR OPTICAL MICROSCOPE.
TERMINAL.
CONDENSER COIL. C.
OBJECTIVE COIL. O
ADJUSTABLE ADAPTOR FOR OPTICAL MICROSCOPE.
OBJECT CARRIER CAM ADJUSTMENT
OBJECTIVE COIL ADJUSTER.
SPRING RETURN.
OBJECT HOLDER.
HEAD ADJUSTMENT
COIL ADJUSTMENT.

FIG. 5 (I^3)
Optical microscope and electron microscope mounted for related working

adequate insulation between layers. It was therefore found necessary to use paper insulation, and to prevent the evolution of gas therefrom by making the shroud gas-tight. The design of the pole-pieces is still a matter of research, so the shrouds have been designed so that the pole-pieces may be removed and replaced in a simple manner. The focal length of the coils can be controlled by varying the current passing through them. Any small departure, either transverse or angular, of the magnetic axes of the coils from the axis of the beam will lead to aberrations. Means are therefore provided so that, without breaking the vacuum, all three coils may be given a transverse movement relative to the beam. Means are also to be provided for the angular adjustment of the condenser coil. Due to the short object-distance of the objective coil, it is necessary after placing the object in position and locating it by means of the object-holder adjustment, to raise the objective coil until the object is surrounded by the shrouding of the coil. The coil is mounted on a special slide which ensures true straight-line motion without sticking and is brought into position by an external adjustment.

Cameras. Two cameras are provided, one at the position of the intermediate image and the other at that of the final image. The upper camera, of the form designed by Finch and Quarrell [1] carries a plate holder and a split shutter, so that either half or the whole of the plate can be exposed. The upper part of the apparatus can be used as an electron diffraction apparatus and the upper camera is used to record images produced by this means. It would also, of course, be used in taking true electron microphotographs when it was desired to use the first stage of magnification only. When it is desired to use the lower camera, the upper one may be swung out of the axis of the beam which then passes on through the third coil.

The lower camera is similar to that designed for use with the high-speed cathode ray oscillograph, but is equipped with a plate holder as well as with the usual facilities for photographic film. Both cameras are fitted with fluorescent screens for visual observations and viewing windows are provided at a suitable angle to the main body. At the start a magnification of about 1,500 was obtained, but this has doubtless been much improved.

Diffraction Adapter. The R.C.A. diffraction unit is an attachment which enables the electron microscope to be used as a diffraction camera. A diffraction adapter which contains a special coil as well as the standard projector coil replaces the original projector coil of the instrument. Specimens for either transmission or reflection study can be mounted in special holders provided with the adapter. For reflection study, the specimen can be moved laterally, circularly, and angularly.

Preparation of Specimens. Instead of the glass slide which is used in light microscopes a thin film of some material like collodion is used. The following is the usual technique. A deep petri dish is filled with one or two inches of distilled water. A 2 per cent solution of collodion or parlodion solution or almost any nitrocellulose in amyl acetate is prepared. Very good results have been obtained with a parlodion solution. A dropper containing some of the solution is held about half an inch above the surface

[1] *Proc. Phys. Soc.*, 1934, *46*.

of the distilled water and a single drop released. This drop will quickly spread over the surface of the water forming a very thin film about 200 Å in thickness. A small 200-mesh screen $\frac{1}{8}$ in. in diameter is then placed on the film and prodded gently to ensure adherence of the film to the screen. A special tool is now placed below the screen and film for the purpose of picking up the screen. Before doing this it is necessary to break the film around the tool by carefully piercing the film with a finely drawn glass rod. The special tool is raised and inverted and is then held over a small cylindrical pedestal where it rests with the film now on top. Excess water is drawn off with a dropper. The pedestal is then returned to its holder and the film allowed to dry.

There is a great variety of ways in which individual specimens can be or should be prepared. Crystalline materials are generally ground into very fine particles with a pestle and mortar and then suspended in distilled water. A tiny drop of the suspension is emitted from a capillary tube on to the dry film supported on the screen. When this has dried sufficiently it is placed in the special specimen holder provided with the specimen downward. The specimen holder is then inserted in the specimen chamber.

Bacteria specimens can be prepared in the same way. A very successful way is to mix the specimen with the collodion before this is dropped on the water to form the film. In some cases the problem is not so simple since in order to permit penetration by the electrons the thickness of the specimen should be less than one-tenth of a micron : even so, successful techniques in thin sectioning have been developed in the study of muscle fibre, &c.

In studying the surfaces of solids such as metals the simplest method is to prepare a thin collodion film on the etched surface of the metal and then remove this film for mounting on a specimen screen. A much better, if slightly more difficult, method is the polystyrene-silica method developed by the Dow Chemical Co. of Midland, Michigan. A polystyrene film is first formed on the etched metal surface. This film is stripped from the metal and gives a negative replica. The polystyrene film is then placed in an evaporating-chamber and some silica is evaporated on to the surface of the polystyrene forming a silica film of molecular dimensions. The polystyrene is then dissolved away, leaving the silica as a positive replica of the metal surface for examination in the electron microscope.

Uses of the Instrument. A few examples may be given. In the field of bacteriology it is known that the diphtheria bacillus reduces potassium tellurite to tellurium ; H. E. Morton and T. F. Anderson[1] were able to show that this change takes place inside the bacteria since minute crystals of tellurium could be seen within the organism. That the crystals were tellurium was established by the fact that they could be dissolved out with bromine water.

Before the advent of the electron microscope practically all viruses were beyond the range of observation. They are thought to be minute particles constituted of organic compounds such as nucleoprotein. Whether they are to be regarded as very elementary living bodies or as inanimate organic molecules is not decided. What is important is that they do cause disease in plants and animals. Stanley and Anderson[1] studied the tobacco mosaic virus. With very dilute suspensions the virus was found to consist of rod-like particles having a width of 15 millimicrons and a length of 280 millimicrons.

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[1] *Proc. Soc. Exp. Biol. & Med.*, 1941, *46*, 272.

An interesting development in the use of the electron microscope concerns the examination of the surface structure of metals. One method employs a precision polystyrene moulding of the surface to be examined, silica being subsequently condensed on the polystyrene surface by an evaporation process; the styrene is removed and the silica, which is claimed to reproduce exactly the surface structure of the original metal surface, is examined by means of the electron microscope.[2] For a review of the application of the electron microscope in metallurgical research see article by Barrett.[3] Results to date indicate that special metallographic polishing and etching techniques are necessary and give better results than ordinary mechanical polishing which often produces too coarse etch pits.

According to Keller and Geisler[4] different types of electron microscopes have been applied to study the structure of metals and alloys.[5] These are (1) the emission type, in which the sample serves as the cathode to furnish electron emission; (2) the reflection type, in which the radiation reflection by the surface of the sample is used to form an image which is magnified by electronic lenses; (3) the scanning microscope in which the surface of the sample is scanned by a very small beam of electrons and the secondary radiation emitted by the sample actuates a facsimile pointer in synchronism with the movement of the electronic probe; and (4) the transmission type, in which the path of the electrons is analogous to that of the light path in the transmission light microscope. The microscope has high resolving power and probably gives the best results with the technique available. Keller and Geisler[6] draw attention to the fact that the transmission type of electron microscope is not adaptable to the examination of metallic samples directly on account of the thickness of the sample. This difficulty, they state, can be overcome in a number of ways; e.g. (1) by the preparation of suitable specimens by the replica method, in which either a negative or positive reproduction of the surface of the sample is obtained on a very thin film; and (2) the oxide film method.[7]

Improved Forms of the Electron Microscope. In recent years there have been many improvements in the design and efficiency of the electron microscope, and brief reference will be made to a few of these. The Radio Corporation of America, for example, have developed at least two new models. One of these, incorporating an electron diffraction camera as a built-in unit, and a smaller console model of a different type without a diffraction unit but with two amplification steps 500 × and 5,000 ×. A built-in camera makes it a simple matter to obtain good micrographs which can be usefully enlarged to 100,000 diameters.

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[1] *J. Biol. Chem.*, 1941, *139*, 325.

[2] See, for example, *J. App. Phys.*, 1943, *14*, No. 1, 23.

[3] *Ibid.*, 1944, *15*, 691.

[4] *Ibid.*, 1944, *15*, 696. [5] *Ibid.*, 1943, *14*, 522. [6] *Loc. cit.*

[7] See Mahl, *Metallwirts*, 1940, *19*, 488.

The New Universal model has many improvements on earlier models with simplification in mechanical and electrical design.[1, 2] It is possible with this instrument to make electron micrographs and electron diffraction patterns of the same specimen in a few minutes. The electron diffraction unit may sometimes be used to identify an unknown substance, or to detect impurities in known material. The electron optical system is contained in a vertical column at the front of the instrument. The air locks of earlier models (for inserting specimens and film plates) are eliminated, due to a more efficient pumping system. This latter consists of a diffusion pump situated in the lower part of the column and a mechanical forepump mounted externally. An anode voltage of 50,000 volts controlled to ± 1 volt is possible. All controls are mounted on a sloping panel in a convenient position. These include controls of magnification, focus and stage positioning. The operator sits in front of the instrument and views the image through the glass windows above the control board. A three to one magnifying glass is mounted so that it can be swung into viewing position. Slide doors cover the windows when a photograph is being taken. The cable release on the panel operates a shutter exposing the plate. Direct magnification can be varied in forty steps from 100 × to 20,000 ×. Resolution is better than 100 Ångstrom units.

Reference should also be made to the greatly improved models of Metropolitan-Vickers. In 1936, for example, they placed on the market a 50-KV model (Type E.M. 2). This instrument employs three magnetic lenses for focusing the 50-KV electron beam.[3] The condenser lens focuses on to the specimen the electrons from the hot cathode gun. The objective lens forms an image of the specimen at an intermediate plane, where it may be viewed on a fluorescent screen. The projector lens further magnifies this image by an amount which can be varied by means of the lens current up to a maximum of 180 times. The final image falls on a 3-in. square fluorescent screen mounted on top of the camera. This screen can be moved out of the beam to allow the image to impinge directly on the photographic plate beneath for the purpose of obtaining a photographic record. The resolving power (better than 100 Ångstrom units) is such as to allow further useful enlargement of the photographic image to give a total magnification of up to 50,000 times.

The high degree of vacuum necessary within the tube is achieved by a continuously-operating oil diffusion pumping equipment of familiar type as developed by the Company. A ‘ Metrovac ’ 03B oil diffusion pump backed by a ‘ Metrovac ’ DR1 rotary pump is used in a completely automatic system, controlled by one switch and two push-buttons. The rotary pump is mounted externally to avoid any mechanical vibration arising from this source affecting the instrument. Interlocks between the units are designed to obviate incorrect operation as far as possible.

Air locks are fitted to the tube to facilitate rapid changing of the specimen and photographic plate. The former operation takes under two minutes and the latter only a little longer. The push-buttons mentioned in the

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[1] R.C.A. Leaflets, Victor Division, Camden, New Jersey.

[2] Wildhack, *Rev. Sci. Inst.*, 1944, *15*, 154.

[3] Metropolitan-Vickers Elec. Co., Manchester, Leaflet, No. 902/17—1, 1946.

previous paragraph operate the valves that control the evacuation of the air locks.

The design of the tube is such as to provide maximum accessibility to all components. The lenses, specimen air lock, camera, &c., can all be removed as individual units without disassembling the main tube. This feature has proved of particular value.

It is necessary to make certain adjustments within the vacuum while the tube is running. These adjustments are made through flexible metallic bellows or special synthetic rubber packed glands which maintain a vacuum-tight joint. In this way the gun may be tilted or moved transversely ; the mechanical stage may be moved to observe different parts of the specimen ; the projector lens may be moved transversely and the air lock shutters, &c., operated. The mechanical stage controls are carried down to a convenient position for comfortable operation while viewing the final image.

The specimen is normally mounted on a very thin plastics film (100 Ångstrom units thick) covering a grid (with a mesh of 200 lines per in.) which is held in a capsule having a conical surface to fit into the mechanical stage.

The 50-KV power supply is obtained from a completely oil-immersed 50 c.p.s. half-wave rectifier unit ; measuring 28 in. × 22 in. × 24 in. high, this can be installed in any convenient corner of the room or under a bench or table. The output is fed through a shielded high-voltage cable directly to the microscope electron gun. The arrangement is such that no part at high voltage is exposed, and the safety of the operator is assured.

The third unit is the control desk, which houses the electronic stabilizing circuits used to stabilize the accelerating voltage and coil currents to 0·002 per cent. Controls are provided to adjust the beam accelerating voltage, the beam current, focusing, magnification, &c. Three meters measure beam current, lens currents and H.T. stabilizer balance respectively. In addition, indicator lamps inform the operator whether or not the vacuum pumps, &c., are in operation.

The Proton Microscope. According to Magnan and Chanson,[1] the electron microscopes using magnetic lenses have now practically reached the theoretical limit of resolving power on the de Broglie wave-length formula. A proton microscope would be able to resolve objects 40 times smaller than can be seen with the electron microscope. If one considers that the true limit of resolution is set by spherical aberration and diffraction, it can be shown that a gain of resolution of 10 times is possible.

In addition, proton microscopes have advantages over electron microscopes in that the influence of parasitic magnetic fields on the beam is negligible and that the relativistic chromatic aberration is very small.

Since the focal lengths of magnetic lenses are too short for protons, a proton microscope can only be electrostatic, and indeed calculations have shown that any electrostatic electron microscope can be converted into a proton microscope by replacing the electron gun by an ion source and reversing the polarity of the power supply.

The problem of obtaining a sufficiently intense monochromatic ion source has been solved in a new way by using ions from that part of a Crookes tube cold cathode discharge such that they had no initial radial velocity. The oscillating electron principle of Hans Heil had also provided a satisfactory source, similar to the Finkelstein proton gun.

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[1] From a Report of the Sixth Conference on the Electron Microscope and its Applications, see *J. Sci. Inst.*, 1948, *25*, 25.

Owing to the low power of protons to penetrate matter, 300 kV. was the lowest accelerating voltage which could be used. Specimens will be examined by reflexion with a very low angle of incidence or by transmission where parts of the object are 10 Å or less in thickness. The proton microscope may also be used for gaseous objects, but in general it will be much more limited in use than the electron microscope.

CHAPTER II^3

PHOTO-PHYSICS

SECTION 1: PHOTOELECTRIC CELLS

(photoelectric effect in general is dealt with in Vol. II, Chap. VI, Section 8)

USE of Photoelectric Cell. The determination of the colour content of a solution can conveniently be carried out by means of the photoelectric cell. Numerous reactions have been followed by colour changes recorded by this means. Iron and manganese have been estimated by such a method.[1] Silicic acid has been determined in the presence of phosphoric acid by Cerney [2] using the ammonium molybdate and citric acid method. A photoelectric method has been used for the determination of silicon in magnesium. The magnesium (0·5 gram) is heated with sulphuric acid (45 ml. [1 : 30]) saturated with bromine. To 10 ml. of this solution are added 5 ml. of water, 1 ml. of 5 per cent aq. ammonium molybdate and 5 minutes later 10 ml. of 8N sulphuric acid and 1 ml. of 0·5 per cent stannous chloride. Then water is added to make the volume up to 50 ml. and the intensity of the colour measured with a selenium photo-cell.[3] Uzel [4] has estimated mercury by a photoelectric method using Berlin blue as an indicator. Cohen [5] estimated lactoflavine by measurement of the fluorescent radiation set up by ultra-violet light. Turbidity in drinking water can also be estimated by a photoelectric method.[6]

Summerson [7] has designed a double-cell photoelectric colorimeter which is made by the Klett Manufacturing Co. of New York. Fig. 1 (II^3) shows the principle of the instrument in which A is a schematic view of the rear half of the instrument, in section from above; B is the view across the line OO in A, looking towards the front of the instrument and C is the wiring diagram of the photoelectric cell circuit.

1 is the housing for the 100-watt projection lamp 2, and light from this lamp activates each of the two ‘ blocking layer ’ photoelectric cells 7 and 8 which are mounted at the rear of individual enclosed compartments 10, the light entering the compartments through rectangular slits 11 in the face of each compartment opposite the photoelectric cell. Through an opening in the top of one compartment the test tube, 6, containing the solution under examination is interposed in the path of light striking one of the photoelectric cells, called the ‘ working cell ’, 7. When this tube is in place, the only light which reaches cell 7 is that which has passed through

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[1] Bendig and Hirschmüller, *Z. analyst Chem.*, 1933, *92*, 1.

[2] *Chem. Obsor.*, 1934, *9*, 121, 138.

[3] Davidov and Malinovskaja, *Zavod Lab.*, 1940, *9*, 964.

[4] *Chem. Zbl.*, 1935, *106*, 2051.

[5] *Rev. Trav. Pays-Bas*, 1935, *54*, 133.

[6] Willer and Heinmann, *Forsch. u. Fortschr.*, 1933, *34*, 490.

[7] *J. Biol. Chem.*, 1939, *130*, 149.

the liquid in the tube, so that the current produced in this cell is a measure of the light-absorbing properties of the solution. The second cell, 8, is called the 'reference cell'; it is continuously activated by the source of light and is in no way affected by the procedure of measurement with an unknown solution. The advantage of using a reference cell is that when potentiometric balance has been once obtained this is quite independent of fluctuations in the intensity of the light source, since these will cause the currents from the working cell and the reference cell to vary in the same proportion. Thus the apparatus can be used on any power supply without regard to any variations in line voltage. 4, 9, and 10 show the housing of different parts of the apparatus.

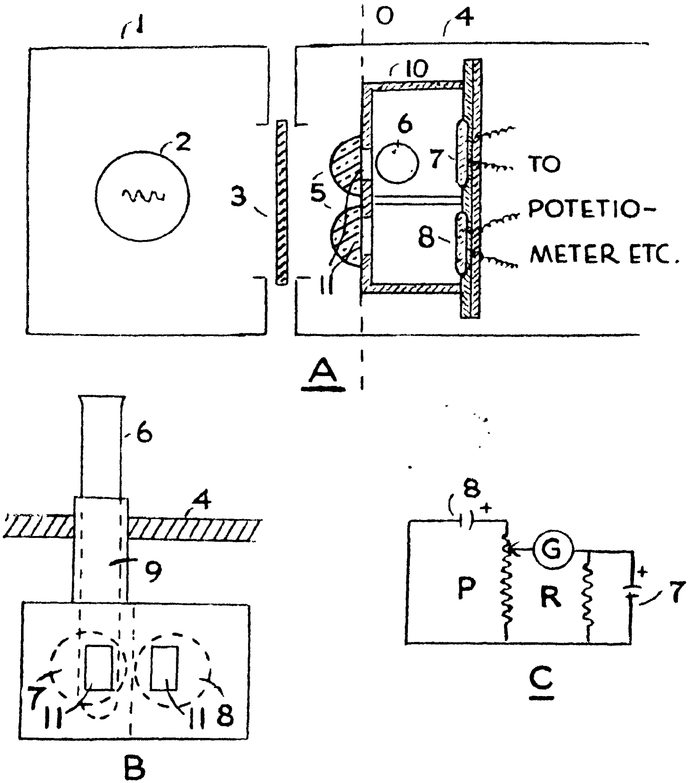

FIG. 1 (II^3)
Summerson photoelectric colorimeter

In the potentiometer circuit, P represents a potentiometer of 400 ohms resistance, R is a fixed resistance of 400 ohms, and G is a low sensitivity galvanometer. The colour measurements are made in terms of the scale attached to the potentiometer. The scale records the position of the sliding contact on the potentiometer wire for its whole length. The reading 0 corresponds to the condition when the whole resistance of P is in the galvanometer circuit. In using the instrument, the fluid under examination is compared with a reference fluid, each being placed in the test tube in turn.

The reference fluid, i.e. the pure solvent or the reagent blank, is placed in the tube and the potentiometer scale is set to read 0.

Zero Adjustment. The establishment of current equivalence for the two cells with the reference liquid in the tube and the scale reading 0 is carried out by moving the colorimeter lamp parallel to the plane containing the two cells. This changes the relative amounts of light striking each cell so that they may readily be brought into exact current equivalence. The alteration in the position of the lamp is brought about by turning the zero adjustment knob, which is located on the side of the lamp housing and is attached to a sliding tube on which the lamp socket is mounted. It is essential that the zero adjustment be made with the tube containing the reference fluid in position since the use of a container of circular cross-section introduces certain factors of reflection and light concentration which will be present in the determination with the ‘ unknown ’ liquid and so must be allowed for now. The lenses shown at 5 partially compensate for these factors. In practice it has not been found necessary to check the determination of the zero after each determination ; equilibrium is reached about 10 minutes after turning on the light and no further change then takes place.

Test Tubes. These are 14 × 125 mm. so that they can be used with volumes of fluid as small as 5 ml. and will fit the ordinary laboratory centrifuge. Scratched or blemished tubes should not be used and they must be clean inside and out. They should be tested for interchangeability with some stable solution by seeing that each in turn gives the same reading in the colorimeter. It is convenient if the tubes are marked at 5 and 10 ml.

Scale. This is graduated in such a way that where measurements are carried out as described, the reading of the unknown solution is measured in terms of the logarithm of the ratio between the photoelectric cell current corresponding to the light transmission of the reference liquid and the current corresponding to the light transmission of the unknown. If these two current values are represented by the symbols i_s and i_r respectively and the scale reading is R, the relation $\log i_s/i_r = 0{\cdot}002$ R holds. The figure 0·002 is an arbitrarily selected convenient factor. The scale from 0 to 200 is marked for each unit of scale reading, from 200 to 300 in two units and so on. A little care is therefore necessary in reading. Duplicate readings with stable solutions are found not to differ by more than 0·3 per cent of the full scale length. By using the logarithm scale the relation between concentration and scale reading is given by $C = kR$, and in comparing solutions of two different concentrations, one being a standard of concentration C_s giving a reading R_s and the other an unknown concentration C_x giving the reading R_x, the unknown concentration is given by

$$C_x = R_x\,(C_s/R_s)$$

Light Filters. It is recommended that these should have a spectral width of 50 to 75 millimicrons. They are mounted on wooden holders and are inserted as shown at 3 in the figure. Glass filters only have been used but it should be possible to use dyed gelatine filters : the light switch is fixed on the housing so that it has to be turned off before a filter is removed. This is because the sudden change from filtered to unfiltered light may require half an hour before the cell settles down again. For the same reason, after changing filters it is well to wait 5 to 10 minutes before again taking readings. The best filter in any individual case can only be found by trial : green or red filters give extreme sensitivity with low concentrations while blue filters give a wide range of proportionality of the concentration ranges most generally encountered.

Photoelectric Colour Measurement of Oils. Two methods in particular use are specified by the American Society for Testing Materials. The Union colorimeter[1] is used for determining the colour of lubricating oils, while light-coloured products are measured with the Saybolt chromometer,[2] which bears no relation to the Union colorimeter except that both depend upon a series of yellow disks and in addition the Saybolt colour involves variation in depth of sample.

A new method using a photoelectric colorimeter has been devised by Diller, Gray, and Wilson,[3] which is accurate and gives easy standardization for the measurement of oil colours. The results can be correlated with those obtained by the standard methods.

The method consists in focusing a stable beam of light into the sample which is held in a standard container. The light is modified by an optical filter and falls on a photoelectric cell. Readings are taken directly from the apparatus scale. One reading is required and a second is optional. The former is taken with the aid of a filter designated as ‘ North Sky ’ or, in the case of very light oils, with a filter designated as ‘ Violet ’. The second reading is taken with a filter designated as ‘ Red ’. The original should be consulted for details of apparatus and methods of working.

Bronstein’s Technique. In colorimetric analysis Bronstein[4] by a photoelectric method uses two photo-cells. One receives light which passes through the solution under examination and the second receives light which passes through a solution which is selected as a control. By changing the aperture of a diaphragm and the galvanometer shunt, and by covering part of a cell by a photofilter, it is possible to achieve the proportionality between the galvanometer reading and $1 - e^{-c}$, where c is the concentration of the unknown solution for a number of values of c. When three values are obtained the proportionality is approximately satisfied for all other concentrations.

Measurement of Enzyme Activity by a Photo-electric Method. In principle, the method depends upon the use of a substrate consisting of a standardized, homogenized suspension of coagulated egg-white.[5] When acted upon by pepsin, the turbidity decreases with time. The amount of protein digested in unit time is proportional to this decrease in turbidity and the turbidity is measured by means of a photoelectric colorimeter. The peptic activity of the system can thus be determined. Protein hydrolysis so measured follows a monomolecular course and hence the enzyme activity can be expressed as a velocity constant. A Klett-Summerson photoelectric colorimeter with a blue-violet (No. 42) filter was employed.

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[1] Amer. Soc. Testing Materials, Standards on Petroleum Products and Lubricants, Designation D155–39T.

[2] *Ibid.*, Designation D156–38.

[3] *Ind. Eng. Chem. Anal.*, 1942, *14*, 607.

[4] *Zavod Lab.*, 1940, *9*, 1070 ; *Brit. Chem. Abs.*, 1944, C. Abs. 468, 46.

[5] Riggs and Stadie, *J. Biol. Chem.*, 1943, *150*, 463.

For the construction of photoelectric photometers and photoelectric absorptiometers see Vol. II, pp. 260–3 and 272–5·2.

Variations in Colour Concentration Recorded by a Photoelectric Device. An apparatus capable of indicating by photoelectric methods the concentration at any instant of a temperature controlled coloured solution has been described by Davenport.[1]

Principle of Davenport's Apparatus. The apparatus provides a means of measuring the light absorption of a dyestuff solution which is being circulated through a mass of textile material. Light from a 12-V, 36-W spotlight bulb is modulated by a rotating sector disk and focused by a lens on the flattened portion of a cross-tube connecting towards their upper extremities the two limbs of a U-tube containing the temperature controlled coloured solution which circulates rapidly through the system under the action of a rotating stirrer.

The fibre under examination is contained in a 3-in. length of glass tubing fitted at the lower end with a perforated porcelain disk allowing free circulation of the dyestuff solution, the whole fitting snugly in the left-hand limb of the U-tube. The light is partially absorbed by the coloured solution circulating through the cross-tube and is then passed through a suitable colour filter and focused on the cathode of a vacuum photo-cell by a second lens. The photo-cell is placed in the anode circuit of a pentode valve so connected that the voltage developed between anode and cathode shall be a logarithmic function of the photo-current. This voltage is applied to the input of a three-stage resistance capacity coupled amplifier, the output of which is rectified by a double-diode, and measured on a galvanometer of low sensitivity inserted in the cathode lead.

The relations between the concentration of dye in the solution and the input voltage of the amplifier are as follows :

$$\mathrm{I} = \mathrm{I}_0 e^{-cx}, \quad i_p = k_1 \mathrm{I}, \quad \mathrm{V} = k_2 \log i_p + \mathrm{A},$$

where I_0 = intensity of light incident upon the solution, I = intensity of transmitted light, c = concentration of coloured solution, x = length of light path through solution, i_p = photo-current produced by light intensity I, V = input voltage to amplifier, k_1, k_2 and A = constants.

It will be seen from these equations that the relation between solution concentration and galvanometer reading should be linear. This is strictly true only when monochromatic light is used but by employing suitable ' spectrum ' filters the relation is obeyed fairly accurately.

Construction of Apparatus. The U-tube is illustrated in Fig. 2 (II^3). The two limbs are 1-in. bore, the cross-arm ¾-in. bore and the narrower tubing connecting the two limbs at the bottom and containing the drain tap is ¼-in. bore. A 1-in. length of ½-in. bore tubing is inserted at the base of the left-hand limb sloping slightly upwards to serve as a pocket for the mercury-in-glass thermostat control. The slope ensures that no liquid is trapped when the U-tube is drained. All glass used is Pyrex.

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[1] *J. Sci. Inst.*, 1944, *21*, 84 and 188. Thanks are due to Mr. Davenport, to I.C.I. (Dyestuffs), Ltd. and the *J. Sci. Inst.* for description of this apparatus and for the electros for related figures.

Towards the base of the right-hand limb, in three deep indents is held a shaped piece of Neoprene which serves as the lower bearing for a $\frac{1}{8}$-in. diameter stainless steel shaft carrying three stainless steel impellors $\frac{7}{8}$ in. diameter. The upper end of the shaft passes through a brass insert in a Neoprene bung fitting tightly into the mouth of the right-hand limb. The shaft ends in a 1-in. diameter brass pulley which is belt-coupled to a small induction motor. Both limbs of the U-tube are wound with two layers of 26-gauge copper wire, each layer being separated from the other and from the tube by thin asbestos string, wound on wet, smoothed and dried to present a hard regular surface for the windings. The total resistance of the windings when connected in parallel is 0·6 Ω and they are fed from a 6-V transformer. By using this low voltage two purposes are served. First there is no possible danger should the heaters accidentally become damp during operation, and second no precautions are necessary to prevent the amplifier being disturbed by the thermostat's make-and-break action when control is effected on the low-voltage circuit. The thermostat control (see Fig. 2 (II[3])) consists of a 1-mm. bore capillary tube, T, ending in a bulb 1 in. long by $\frac{3}{8}$ in. diameter which is inserted in the side arm at the base of the U-tube. The adjustable contact to the mercury surface is secured to a spring-loaded collar which slides on a steel shaft and is actuated by a 3 : 1 reduction lever the end of whose long arm traverses a scale, K, calibrated in degrees Centigrade. The thermostat operates a simple valve relay which controls the 10-A current taken by the heating coils of the U-tube with the aid of a Sunvic hot-wire vacuum switch.

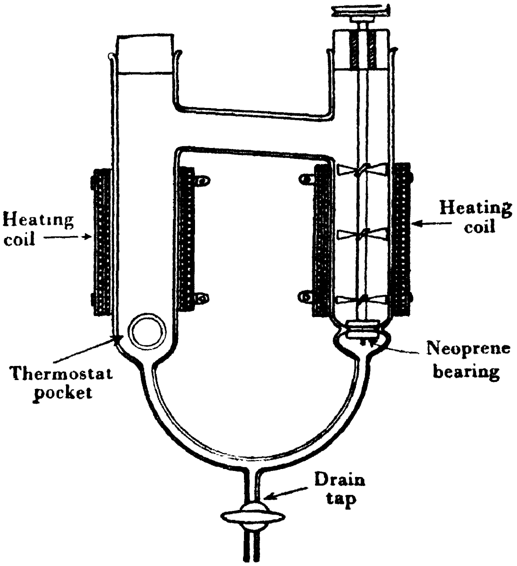

FIG. 2 (II[3])
U-tube of photoelectric device for recording variations in the concentration of a coloured solution

The optical system is shown in Fig. 3 (II[3]). Rigid mounting is essential owing to the vibration from the motors. The light beam is modulated at approximately 300 cyc./sec., but the frequency is unimportant and may be varied within wide limits. Since the amplifier has very little frequency discrimination, variation in speed of the modulator disk due to mains voltage fluctuations has no effect on the output.

The colour filters, F, used are Ilford Spectrum Filter Nos. 601–8. The intensity of the lamp is kept constant by feeding the lamp transformer from a constant voltage transformer supplied by Advance Components Ltd. It should be mentioned that in order to deal satisfactorily with the high optical densities encountered in some of the dye solutions examined it was found necessary to flatten the cross-arm of the U-tube to give an optical path in the liquid of approximately $\frac{1}{8}$ in.

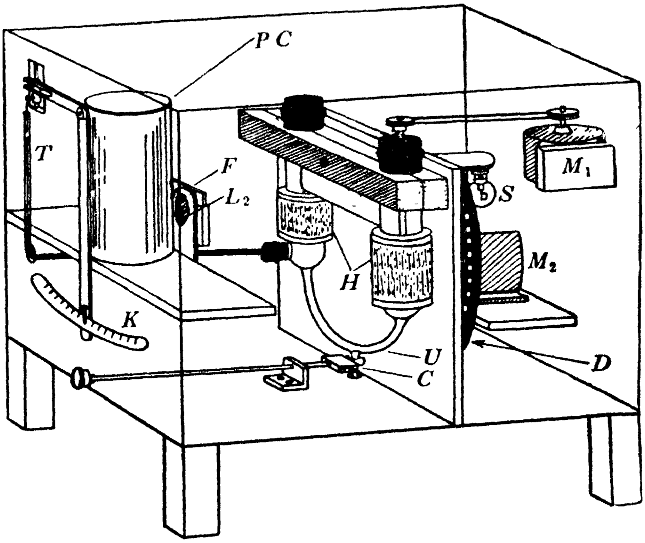

FIG. 3 (II³)

A photoelectric device for recording variations in the concentration of a coloured solution
C, draincock ; D, modulation disk ; F, colour filter ; H, heater coils ; K, thermostat scale ; L_2, second lens (L_1 situated between modulation disk and U-tube) ; M_1, circulation motor ; M_2, modulation motor ; PC, photo-cell ; S, light source ; T, thermostat capillary ; U, U-tube

The logarithmic amplifier is based upon the circuit devised by Meagher and Bentley.[1] A pentode valve, type 6J7, is used, the three grids being strapped together and maintained at a potential of 50 V above that of the cathode. The anode is connected through a 2 MΩ resistance to the cathode of the vacuum photo-cell (type KMV6), of which the anode is maintained at a potential of 70 V. In order to limit the grid current, the cathode is run considerably below its normal working temperature by dropping the heater voltage through a variable 20 Ω resistance. The three grids are supplied through a 100,000 Ω resistance from the 350-V high-tension supply and the heater resistance is adjusted till the grid current is 3 mA, the normal cathode current for the 6J7. The circuit diagram is shown in Fig. 4 (II³) together with the rest of the amplifier which is a normal resistance-capacity coupled type with a gain of about 100 db. utilizing a further three 6J7 pentodes and a D63 double-diode rectifier. By means of the potentiometer shown in Fig. 4 (II^3) the cathode voltage of the D63 may be varied between 0 and 50 V above ground potential, thus enabling small ranges of solution concentration to be examined over the full range of the galvanometer scale. The amplifier is fully screened and enclosed in an earthed metal case, connexion with the photo-cell being made by a two-way screened cable.

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[1] *Rev. Sci. Instr.*, **1939**, ***10***, **336**.

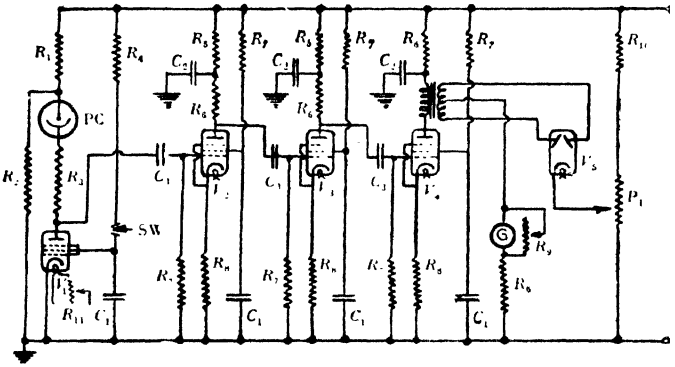

FIG. 4 (II^2)

Circuit diagram of logarithmic amplifier

R_1 = 40,000 Ω
R_2 = 10,000 Ω
R_3 = 2 MΩ
R_4 = 100,000 Ω
R_5 = 50,000 Ω
R_6 = 250,000 Ω
R_7 = 1 M Ω

R_8 = 2,000 Ω
R_9 = 0–200 Ω
R_{10} = 60,000 Ω
R_{11} = 20 Ω
P_1 = 10,000 Ω
C_1 = 0·1 μF

C_2 = 4 μF
C_3 = 0·01 μF
V_1 = V_2 = V_3 = V_4 = type 6J7
V_5 type D63
PC = KMV6 photo-cell
SW = single-pole switch

Power for all circuits in the apparatus is taken from the mains, the d.c. necessary for the amplifier being obtained from a standard design power pack using full-wave rectification and efficient filtering arrangements. The input to the power pack is taken from the constant-voltage transformer which feeds the 12-V transformer supplying the light source. The valve relay, the 6-V heater transformer and both the small induction motors run directly from the mains.

The disk modulator, D, U-tube with mercury thermostat, heating coils, H, circulator and screened photo-cell, PC, are mounted together as shown in Fig. 4 (II^3). The amplifier (which is totally enclosed in an earthed metal case) and the chassis containing the remaining equipment (comprising the amplifier power pack, constant voltage transformer, valve relay, 6-V heater transformer and 12-V lighting transformer) are each mounted separately. By this division the amplifier is protected from the vibration due to the motors and the magnetic fields arising from the various transformers.

Operation of Apparatus. Equilibrium temperature is reached by the cathodes of the amplifier valves 15 minutes after switching on and the apparatus is then ready for use, variations in the gain of the amplifier being less than 1 per cent over a period of 8 hours. It is important, however, that no voltage be applied to the grids of the logarithmic valve until 5 minutes after the amplifier has been switched on ; failure to observe this precaution results in erratic behaviour extending in extreme cases over a period of some 2 hours. For this reason a switch is included in the grid circuit of the logarithmic stage. After a preliminary ' warming up ' of the amplifier (during which period the dyestuff solution can be raised to and held at the desired temperature) and the setting of the two amplifier controls the glass tube containing the fibre is inserted into the U-tube and thereafter galvanometer readings taken at suitable intervals of time. The calibration of the apparatus is carried out at the end of a determination. Some evidence of the accuracy and reproducibility of the determinations made by means of this instrument can be gathered from the appended table which shows the percentage exhaustion of the dyebath obtained during four repetition dyeings. The dye solution used was an aqueous solution of Chlorazol Green BN125 at a concentration of 0·26 g./l. Measurements carried out on this solution using the Hilger photoelectric absorptiometer indicated that its optical density under similar conditions to those encountered in the apparatus under discussion was 1·8. Tests carried out to determine the limiting optical density which could be handled by the apparatus gave a figure of 3·5.

TABLE OF PERCENTAGE EXHAUSTION OF DYEBATH, SHOWING REPRODUCIBILITY OF RESULTS

Time (min.)	Per cent exhaustion			
	A	B	C	D
1	15	15	15	15
2	23·5	24	24	25·5
4	35·5	36	37·5	38
8	51·5	49·5	51·5	51·5
12	60·5	57·5	60·5	61·2
20	66·5	67·0	67	67·0
30	69·5	70·5	70	70·5
45	71·25	71·25	71·75	72·0

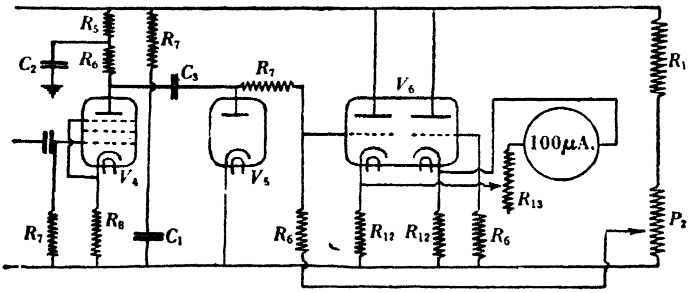

FIG. 5 (II³)

$R_5 = 50{,}000\ \Omega$
$R_6 = 250{,}000\ \Omega$
$R_7 = 1\ M\Omega$
$R_8 = 2{,}000\ \Omega$
$R_{12} = 900\ \Omega$
$R_{13} = 20{,}000\ \Omega$
$R_{14} = 200{,}000\ \Omega$
$P_2 = 2{,}000\ \Omega$
$C_1 = 0{\cdot}1\ \mu F$
$C_2 = 4{\cdot}0\ \mu F$
$C_3 = 0{\cdot}01\ \mu F$
V_4 = type 6J7
V_3 = type D63
V_6 = type 6FB

A modified apparatus simpler to use has also been described by Davenport.[1] In the original apparatus the voltage output from the amplifier was rectified by a double diode, the resulting direct current being read on a galvanometer and in order to 'zero' the galvanometer variable voltage biasing was applied to the diode. It is possible to over-bias the diode without the error showing on the galvanometer. In the modified apparatus this defect is eliminated (Fig. 5 (II^3)).

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[1] *J. Sci. Inst.*, 1944, *21*, 188.

The logarithmic stage and the three-stage resistance capacity coupled stages remain the same, but a balanced peak reading valve voltmeter circuit is substituted for the diode.

Alkali Photo-cell. In Fig. 6 (II^3) a metal plate negatively charged is connected with a small gold-leaf electroscope. When the light from a sodium or mercury vapour lamp falls on the plate the leaves of the electroscope collapse. The plate loses electrons under the influence of the light.

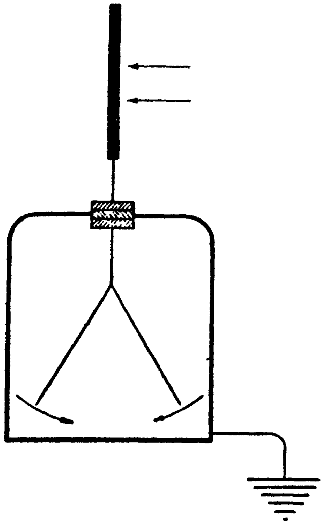

FIG. 6 (II^3)
Gold-leaf electroscope connected with charged metal plate

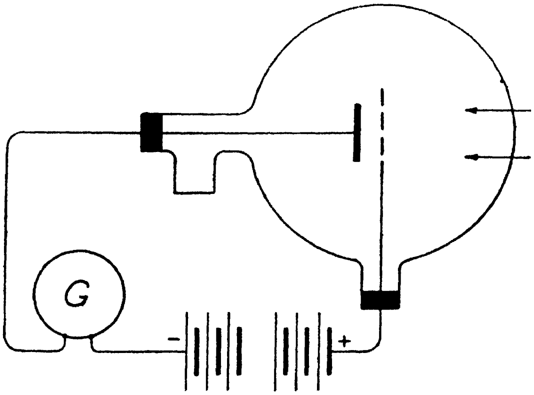

FIG. 7 (II^3)
A simple alkali photo-cell

A simple form of alkali photo-cells is shown in Fig. 7 (II^3). Alkali metal is contained in an evacuated bulb and connected to the negative pole of a battery, and the wire net with the positive pole. On irradiation of the alkali an electron current flows from the photo-cathode to the anode. The particular rays from the alkali metals are between the infra-red and part in the visual region, as far as the green region of the spectrum.[1]

Rectifier or Barrier-layer cells have the great advantage that they give larger currents than the photo-cathodes and that they do not need auxiliary high tension. Thus it was possible to construct photographic pocket exposure and portable light intensity meters of all wave-lengths (including X-rays) for eye observation and with recording equipment. Several books [2] have been published dealing with the wide and ever-increasing field of application of these cells.

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[1] Lange, *Photo-elements and Their Application* (translated by Ancel St. John), Reinhold Pub. Co., 1938, should be consulted for detailed account of photoelectric cells and their application.

[2] e.g., Lange, *Die Photoelements und ihre Anwendung,* 2 parts. Leipzig, 1936. English translation by Ancel St. John, Reinhold Pub. Co., New York, 1938.

Sulphur Thallium Photo-electric Cells. [1], [2] A very sensitive cell can be made with dithallium sulphate. The average sensitiveness is 5,000 micro-amperes per lumen with light from a tungsten lamp at 2,840° absolute.

Purified thallium and double sublimed sulphur mixed in correct proportions for the compound dithallium sulphide are placed in a test tube of heat-resisting glass and sealed off under a vacuum of 10^{-4} mm. of mercury. It is heated very slowly (to avoid an explosive reaction) to 600° and kept at this temperature for several hours. To make the black crystalline mass a good photo-electric material it must contain an admixture of thallium oxide Tl_20. The foundation plate is made of iron to the underside of which is welded a nickel wire to act as conductor. A deposit of dithallium sulphide and thallium is fixed by sublimation on the iron plate. Mild oxidation forms a layer of photo-sensitive material (dithallium sulphide with a trace of dithallium oxide) slightly thicker than the minimum necessary to absorb the light superimposed upon a layer of dithallium sulphide and metallic thallium.

The upper electrode has a semi-transparent layer of gold. The second conductor consists of a sheet of tin-foil clamped to the foundation plate by means of a phosphor-bronze spring with a paper insulating layer between the spring and the tinfoil. The plates are varnished with styrolene dried and then sealed in a vacuum of 10^{-4} to 10^{-5} of mercury and subsequently filled with hydrogen at 300-400 mm. of mercury.

Photochemical Oxidation of Alcohol. Alcohol alone is not oxidized by the action of light, but in presence of oxalic acid, photochemical oxidation can occur [3] with the formation of formic acid, acetic acid, and carbon dioxide. Cohen [4] showed that in the photochemical oxidation of alcohol to acetic acid the action is independent of the quantity of ketone present. In the formation of aldehyde in plant organisms the view is held that it is a secondary reaction due to the photochemical oxidation of alcohol.[5]

[1] Kolomietz, *The Brit. Chem. Digest*, 1947, *2*, 8; Zhurnal Tekh, *Fisiki*, Russia, 1947, *27*, 195.

[2] Tika Asai, *Bull Inst. Phys.-Chem. Res., Tokyo*, 1940, *19*, 415.

[3] *Sernagiotto Atti Accad. Lincei*, 1919, *28*, 1, 436; *Chem. Abs.*, 1920, *14*, 1672.

[4] *Proc. Acad. Sci. Amsterdam*, 1919, *28*, 436.

[5] Stoklasc and Bares, *Chem. Abs.*, 1928, *22*, 2388. See also Morris, *Chem. Reviews*, 1932, *10*, 483.

SECTION 2: FLUORESCENCE

When light rays (especially short-wave radiation) fall on a substance and the emitted light shows a difference from the incident light (e.g. in colour) the phenomenon is known as fluorescence. The short-wave radiation causes an electronic transmission in the molecules or atoms of the substance which take on an excited state. This excess energy may disappear in collisions between atoms or molecules. On the other hand, the electrons may very rapidly return to a lower level and a radiation of a frequency corresponding to the difference of the initial and final electron levels is emitted. The result constitutes the phenomenon known as fluorescence.[1]

Among inorganic compounds it is observed in uranium and rhodium salts. Platinocyanides of barium, magnesium, and potassium also show fluorescence in the solid state. Mercury and sodium vapours under certain conditions show the phenomenon. A well-known example is the organic compound fluorescein. This substance, dissolved in alkali, gives a green fluorescence. Fluorescent dyes are obtained from many derivatives of 1 : 3 dihydroxy-benzene in which the position 5 is unoccupied. When an organic substance is exposed to ultra-violet light (for example to the light from a mercury vapour lamp, from which most of the visible rays have been removed by suitable glass filters) fluorescence occurs in many cases. In only a small number of instances is this phenomenon easily observed. The following table has been prepared by Campbell.[2] It records a number of organic products which show the phenomenon readily in ultra-violet light :—

Substance	Effect
Benzene	Feeble violet
Stilbene	Blue-violet
Naphthalene (para)	Slight violet
2–3 dimethyl-naphthalene	Blue-violet
2–7 dimethyl-naphthalene	Feeble violet
Anthracene (pure)	Bright blue
Anthracene (technical)	Bright green-yellow
Phenanthrene	Violet
Fluoranthrene	Brilliant green
1–2 benzanthracene	Blue
2–3 benzanthracene	Orange
Pyrene	Brilliant green-yellow
Chrysene	Bright violet
Perylene	Bright orange-red
Carbazole (technical)	Brilliant violet
Carbazole (pure)	Feeble violet

Kuhn and Wagner-Jauregg[3] found that riboflavin (vitamin B_2 or G) concentrates gave a yellowish green fluorescence upon activation by light of certain wave-lengths. Since this discovery numerous methods depending on the measurement of this fluorescence or on the fluorescence of its degradation products have been employed to measure the amount of this vitamin in various foodstuffs. Thiamin (vitamin B_1) on oxidation gives thiochrome which has a fluorescence. Jansen[1] measured this fluorescence and so indirectly estimated the thiamin.

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[1] For a theoretical review of the subject see Glasstone, *Text Book of Physical Chemistry*, Macmillan, 1940.

[2] *Endeavour*, 1946, *5*, 155.

[3] *Ber.*, 1933, *66*, 317.

The phenomenon of fluorescence has been much used for some years for the qualitative examination of materials and more recently has been adapted for quantitative work as, for example,[2,3] in the estimation of Vitamin B_1, and of Vitamin B_2. Instruments such as the Guild Colorimeter and the Kober Nephelometer have been used for visual work but the tendency is to rely on instruments using the photoelectric cell and in particular those using a null method in which the currents from two photoelectric cells are balanced, since these are independent of fluctuations in the intensity of the light from the mercury lamp which is generally used as the exciting source. Hilger's Spekker Fluorimeter is an example of such an instrument. Here two beams of light from a single source are used. One beam passes through suitable filters and through a variable but uncalibrated sector on to the first photo-cell : the other passes through filters and a variable calibrated sector and is concentrated on to the solution contained in a glass cell : the fluorescence produced passes laterally through filters to the second photoelectric cell. The two photoelectric cells are connected differentially to a sensitive galvanometer. The arrangement may be seen from the diagram (Fig. 8 (II³)). Here S is a compact projector type mercury lamp, the beam on the left passes through the Wood's glass or other suitable filter F_1, ; A_2 is the uncalibrated sector and P_2 is the compensating photo-cell. The beam on the right passes through the filter (Wood's glass), F_1, and A_1 is the calibrated sector. L_1 and L_2 are lenses which form an image of the source inside the cell C which contains the fluorescent liquid. Close behind the cell C is mounted the barrier-layer photo-cell P_1, as shown at the right of the diagram ; here the filter F_2 absorbs ultra-violet light scattered by the

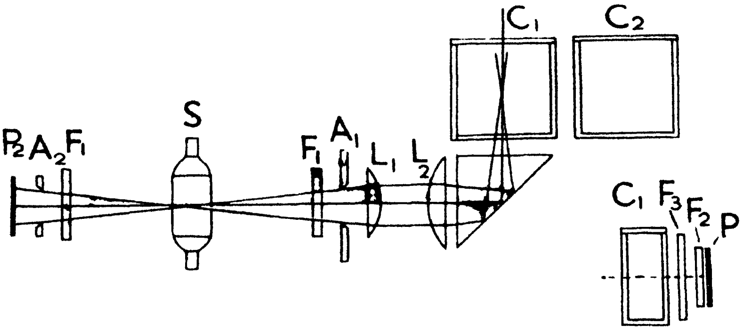

FIG. 8 (II³)
Two photoelectric cells connected differentially to a galvanometer.

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[1] *Rec. Trav. Chim.*, 1936, *55*, 1046.
[2] Jansen, *Rec. Trav. Chim.*, 1936, *55*, 1046 ; Booth, *J.S.C.I.*, 1940, *59*, 181.
[3] *Ind. Eng. Chem. Anal.*, 1937, *9*, 523.

solution and F_3 is a colour filter. The mirror galvanometer to which the two photo-cells P_1 and P_2 are differentially connected has a sensitivity of 2,000 mm. per $\mu\alpha$. Two cells C_1 and C_2 are mounted on a slide so that either can be placed in the path of the beam : a movable cover protects the two cells from external light and the rest of the apparatus is enclosed.

Method. The solution of smaller fluorescence is first placed in the beam with the aperture A_1 fully open ; the aperture A_2 is then reduced until zero deflection is obtained in the galvanometer. Next the cell containing the stronger fluorescing solution is placed in the beam and the aperture A_1 is reduced till zero deflection is again produced. The scale reading of the calibrated aperture gives the ratio of the two fluorescence intensities. For determining the concentration of solutions of varying concentration the instrument must first be calibrated by measurement of several known concentrations in one cell, with a suitable reproducible standard solution of constant concentration in the other. In some cases a piece of fluorescent glass may be used as the standard.

Factors affecting the estimation of concentration by the fluorescence method are discussed by Lothian.[1] The most important are (1) absorption of ultra-violet (or visible) radiation by the substance under estimation ; (2) absorption of the incident radiation by other substances in the solution ; (3) the presence of other fluorescing material in the solution ; and (4) chemical action of impurities with the fluorescing material and quenching due to inorganic salts and the effects of *p*H variation. An increase in concentration generally increases the intensity of fluorescent radiation when the concentration reaches such a value that all the incident radiation is absorbed, a further increase in concentration can produce no increase in fluorescence and this no longer gives any measure of the concentration.

If the total intensity of the fluorescent radiation F emitted is proportional to the total light absorbed

$$F = AI_0\,(1 - 10^{-\varepsilon cl})$$

where ε is the extinction coefficient of unit concentration of the fluorescing material, c is its concentration and l the length of the path in the solution. Hence if F is plotted as a function of the concentration, the curve is a straight line for small concentrations, when the density of absorption of the solution is less than 0·01, that is, when only about 2½ per cent of the incident radiation is absorbed to produce fluorescence.

Also the greatest accuracy in determination of concentration is obtained when the density of absorption of the solution, for the radiation inducing the fluorescence, is equal to 0·43. In practice, errors of this order arise due to variations in the fluorescence of the solutions, so that the solutions need only be made so concentrated as to give an accuracy of 1 per cent, and this means that the linear part of the curve is used.

The Effect of Impurities. When these absorb part of the ultra-violet light, less is available to produce fluorescence. The equation given above then becomes

$$F = \{\varepsilon/(\varepsilon + \varepsilon')\}\,AI_0(1 - 10^{-(\varepsilon+\varepsilon')cl})$$

where ε' is the extinction coefficient of the (non-fluorescing) impurity.

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[1] Lothian, *J. Soc. Chem. Ind.*, 1942, *61*, 59.

This equation on expansion gives

$$F = 2{\cdot}3 \quad AI_0\{\varepsilon cl - 2{\cdot}3\varepsilon(\varepsilon + \varepsilon')cl/2^1, \ \&c.\}$$

When ε and ε' are small, the second term is negligible and the fluorescence is given by the first term only : that is, it is proportional to the concentration and the impurity does not interfere. Hence in general if it can be shown that the fluorescence is proportional to the concentration it may be assumed that the impurities present are not causing any error. If the amount of impurity is so large that its effect cannot be ignored, it may not be possible to dilute the solution to such an extent that it becomes negligible, because this may reduce the fluorescence to too small a value. Experiment and the equation both show that, for a constant and appreciable amount of impurity, the fluorescence is proportional to the amount of the fluorescing material when this is small. This is the basis of the method used by Hills [1] and Booth [2] for vitamin B_1 and by Hobson and Norris [3] for vitamin B_2. In this method an equal amount of the fluorescing impurity is added to the solvent and the solution and the increase in fluorescence in each case is measured ; if this is F_1 and F_2, the factor F_1/F_2 is obtained by which the measured fluorescence must be multiplied in order to correct for the effect of the impurity.

Fluorescing Impurities. When impurities fluoresce in a different part of the spectrum from the substance under measurement, a colour filter is placed in front of the photo-cell to absorb the unwanted fluorescence. For instance, in the estimation of thiochrome, Wratten filters 49 or 47 may be used with the 2A filter which is permanently in front of the photo-cell : the measurements must be corrected as above for the absorption of the ultra-violet radiation.

Choice of Wave-lengths for Irradiation

Generally absorption over a wide band of wave-lengths will produce fluorescence, but sometimes a fluorescing impurity is present which is excited by only a part of that band ; in such a case the choice of wave-length becomes important. Riboflavin absorbs from 4,500 Å down into the ultra-violet ; a test was made with a Spekker fluorimeter using the mercury lines as given below.

Wave-length : filter used :	3,560 Å Wood's glass	4,050 Å Wratten 2 ; Chance 8	4,360 Å Wratten No. 50
Relative intensity of fluorescence .	6·0	1·0	1·8

Here the wave-length 3,560 Å would be the choice if no impurity were present, but in practice with riboflavin impurities are generally present which have a greater fluorescence at 3,560 Å than at 4,360 Å and it is better to use the latter wave-length.

Fluorescence Quenching. A review of the phenomena of extinguishing or quenching of fluorescence has been made by Bowen.[4] This effect was first noted by Buckingham [1] on the addition of certain substances to fluorescent solutions.

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[1] *J. Biochem.*, 1939, *33*, 1966.

[2] *J. Soc. Chem Ind.*, 1940, *59*, 181.

[3] *J. Biol. Chem.*, 1939, *131*, 621.

[4] *Quarterly Reviews*, Chem. Soc., 1947, I.

According to Bowen there are three types of quenching process to be expected : internal, external or collisional, and inner filter or compound type. The theoretical significance of these different types, on the assumption that fluorescence is always due to strong molecular interactions, is discussed in Bowen's review.[2]

The intensity of fluorescence is strictly proportional to the amount of light absorbed, according to Bowen.[3] For analytical work dilute solutions are employed, where the fraction of light absorbed, and hence the fluorescence, is sensibly proportional to the concentration of fluorescent substance, or should be. When two solutions with concentrations in the ratio of 2 : 1 are compared, however, often the fluorescent intensity ratios are less than 2 : 1. For very dilute solutions this error may arise from fluorescence of the glass cells, unwanted scattering, &c. In stronger solutions there may be a real deviation from the 2 : 1 ratio of intensities, owing to the effects, described below. The term ' quenching ' is best restricted to cases where a real non-proportionality of fluorescence to concentration in dilute solutions exists, and may be defined as any effect reducing a fluorescence efficiency below unity. On this view all non-fluorescent coloured substances are 100 per cent quenched. With this definition the molecular picture of the quenching process can be classified into a number of types : (1) Intramolecular effects. (2) Intermolecular effects : (*a*) Bimolecular collisions, (i) with solvent molecules, (ii) with solute molecules, i.e. with added ' quenchers ' or with other molecules of the fluorescent substance. (3) Inner filter action of solvent or added substances.

The quenching of fluorescence in solutions is often accompanied by photochemical reactions, e.g. in the formation of dianthracene on illumination of concentrated anthracene solutions.[4]

The fluorescence of solid solutions (e.g. anthracene-naphthalene) is also dealt with by Bowen.[5] When excited by 3,650 Å light, pure crystalline anthracene fluoresces blue-violet. A very small amount of naphthacene, in solid solution in the crystals, even as little as 10^4, largely suppresses the anthracene emission and changes the fluorescence to the green bands characteristic of the naphthacene. The extinction coefficients show that this cannot be explained as a primary light absorption by the naphthacene molecules, or a secondary absorption of the anthracene fluorescence. The excitation energy of an anthracene molecule after light absorption must be imagined to wander from molecule to molecule in the oriented crystal lattice by a process of resonance. The peculiar sensitivity of the fluorescence of crystals to traces of certain substances in solid solution means that greater caution is required here than for liquid solutions in drawing conclusions of an analytical or purity nature from the observed fluorescence.

Fluorimetric Analysis. An application of this type to the study of Pterins has been made by Simpson [6] by means of which it is possible to demonstrate the presence of pterins in various complex mixtures.

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[1] *Z. physik. Chem.*, 1894, *14*, 129.

[2] *Loc. cit.*

[3] *Analyst*, 1947, *72*, 380.

[4] Weigert, *Naturwiss*, 1927, *15*, 124.

[5] Bowen, *Trans. Faraday Soc.*, 1939, *35*, 15.

[6] *Analyst*, 1947, *72*, 382.

CHAPTER III[3]

ATOMIC WEIGHTS

SECTION 1: METHODS OF DETERMINATION

THE importance of the accurate determination of the relative atomic weights of the elements needs no emphasis, since the closely related quantities, the equivalent weights, or combining weights are the basis of most of the calculations used in analytical chemistry. In addition, one who wishes to become a good analyst could not do better than devote his attention to a thorough study of the methods which have been used by such workers as Stas, T. W. Richards, Baxter, and Noyes, for nowhere else will such a complete study be found of the errors which may arise in the course of analysis and the methods by which these errors may be overcome.

The Chief Methods. The most important of the methods by which accurate values may be obtained are three in number:

1. Methods based upon the determination of the equivalent weights.
2. Methods based upon the X-ray mass spectrum.
3. Methods based upon the limiting densities of gases (*see* Section 2).

Subsidiary Methods. Methods which do not themselves give such accurate values as the foregoing but which are nevertheless of considerable value in confirming the atomic weights are the following:

1. The method depending upon Cannizzaro's view that the gram atomic weight is the least weight found in one gram-molecular weight of any of its gaseous compounds.
2. The method depending upon the generalization of Dulong and Petit that except in the cases of non-metals of low atomic weight the product of the atomic weight and the specific heat is approximately 6·4.
3. Considerations based upon the position of the element in the Periodic classification.
4. Conclusions drawn from Mitscherlich's law of Isomorphism.
5. Values calculated from the series lines of spectra.
6. Calculations from the transparency of the elements to X-rays.
7. Values obtained from the molecular weight and the atomicity—the latter being found from the ratio of the two specific heats of the gas by measurements of the velocity of sound.
8. In a few cases useful evidence is obtained from information derived from the structure of crystals of substances as revealed by X-ray analysis.

The Unit for Comparison of Atomic Weights. The atomic weight of an element is a relative number and therefore has to be referred to some particular element as standard. The element chosen for this purpose by Dalton and Higgins as the lightest of the elements, was hydrogen, to which was assigned the value one. Most of the elements, particularly the metals, do not form compounds with hydrogen which are suitable for atomic weight determinations so that the system of Berzelius in which the atomic weight of oxygen was taken as 100 superseded the hydrogen unit and remained in use for many years. When Dumas carried out his classical research on the gravimetric composition of water in 1842,[1] he found the value 15·96 for oxygen compared with 1 for hydrogen and the nearness of this figure to the whole number 16 made him consider that the latter figure was probably the correct value. Stas for the same reasons as Berzelius favoured the use of oxygen as the standard with the value 16 but the small change in altering the accepted figures in the ratio 15·96 to 16·00 caused his views to receive little support until about 1890 when it was realized that Dumas' figure 15·96 was too high, the correct value being 15·88 ; this figure differs from 16 by nearly 1 per cent so that, largely due to the advocacy of Ostwald, the standard was finally changed to $O = 16{\cdot}000$, the figure which has been retained up to the present day. In practice, determinations are not frequently made by direct comparison with oxygen but more frequently with the halogens.

F. W. Clarke [2] has made a very careful examination of the atomic weights for the eleven elements for which the values are probably known with the greatest accuracy ; these elements are H, C, N, S, Cl, Br, I, Li, Na, K, and Ag. These eleven elements are related to each other by 71 carefully determined ratios, and from these he derived 43 values for the atomic weight of silver, 32 for chlorine, 22 for nitrogen, 16 for bromine, and so on. It is clear, then, that other things being equal, there is an advantage in determining the direct ratio with silver when this is possible.

The Basis of the Analytical Method

The method consists first in the determination with all possible accuracy of the combining weight or equivalent weight with one of those elements whose combining weight (compared with $O = 16{\cdot}000$) is accurately known. The second step is to determine the formula of the compound which has been used or, what comes to the same thing, the valency of our element in this compound. It is then possible to calculate the atomic weight. An example will make this clear. Richards and Baxter [3] converted a quantity of iron into ferric oxide and heated this in excess of oxygen until it would combine with no more. The ferric oxide was weighed, completely reduced in hydrogen and the resulting iron weighed. The results obtained are shown in the table :

Grams of oxide	Grams of iron	Per cent of iron in oxide
3·97557	2·78115	69·956
4·89655	3·42558	69·959
4·35955	3·04990	69·959
7·14115	4·99533	69·951
6·42021	4·49130	69·956
	Mean	69·956

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[1] *Compt. rend.*, 1842, *14*, 537. [2] *Mem. Nat. Acad. Sci.*, *16* (3), Part V, p. 116.
[3] *Prac. Am. Acad. Arts Sci.*, 1900, *35*, 253.

If we knew the formula of the oxide was Fe_2O_3 we could calculate what weight of iron would combine with 1·5 gram atoms of oxygen and this would be the gram atomic weight of iron. The experiment tells us that

30·044 grams of oxygen are combined with 69·956 grams of iron
Therefore 1 gram of oxygen is combined with $\frac{69\cdot956}{30\cdot044}$ „ „ „
and 24 grams „ „ are „ „ $\frac{69\cdot956 \times 24}{30\cdot044}$ „ „ „
i.e. 24 „ „ „ „ „ „ 55·883 „ „ „
and 55·883 is the atomic weight of iron

If we did not know the formula we should then have to make use of one of the methods of determining an approximate value for the atomic weight, e.g. Dulong and Petit's generalization that the product of the atomic weight and the specific heat is approximately 6·2. The specific heat of iron is 0·115 and therefore the atomic weight of iron is approximately $\frac{6\cdot2}{0\cdot115} = 54$.

Richards and Baxter's results show us that 18·6276 grams of iron combine with 8 grams (1/gram equivalent weight) of oxygen. The equivalent weight of iron is then 18·6276 and the atomic weight will be this number multiplied by 1, 2, 3, or 4, &c., according as the formula is Fe_2O, FeO, Fe_2O_3, FeO_2, &c., i.e. the atomic weight is either

18·6276, 37·2552, 55·8828, 74·5104

Knowing that the value is approximately 54, it is easy to decide that the exact value is the third of the above, viz. 55·883 and the formula is Fe_2O_3.

From the example it will be seen that the approximate value may be in error by several per cent and yet leave no doubt as to the correct value for the atomic weight: everything depends on the correctness of the original analysis. It is therefore desirable to consider some general considerations on the accuracy of analysis.

Errors to be avoided in Exact Analyses.[1] The first step must be the choice of a suitable method of experiment and this involves a thorough study of the chemistry of the element in question since much time could be wasted in working with unsuitable material.

Marignac [2] and Stas [3] realized that there were four essential requirements that must be satisfied. These are: (1) the compound which is chosen for analysis is one which can be obtained in an absolutely pure state; (2) the other elements in the compound must each be among the list given of those for which the atomic weight is known with great accuracy; (3) in elements with a variable valency the chosen compound must be one in which we can be certain that the whole of the element is exerting only one of its valencies, thus a ferrous compound in order to be suitable must be obtainable quite free from the ferric salt; (4) the chosen compound must be capable of exact analysis or of exact synthesis.

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[1] See Carnegie Institute Memoir by T. W. Richards, 1910, 125.

[2] *Œuvres complètes*, Geneva, 1902.

[3] *Ibid.*, Brussels, 1894.

The next step is the preparation of the substance in a sufficient quantity and in a pure condition. The amount of material required is from 5 to 50 grams. In most of the work done at Harvard the accuracy arrived at was 1 in 100,000; using 10 grams of substance this would involve weighings correct to 0·0001 gram. If only 1 gram was used the weighings would have to be correct to one-hundredth of a milligram, so that 1 gram is not enough. Stas in some of his experiments used as much as 400 grams of silver in one determination, hoping to get increased accuracy; no doubt the accuracy of the weighings was increased but this did not help him, since his silver was not purified to the same extent and it must be remembered that the error of the final result is equal to the largest of the individual errors. Such large amounts are unnecessary and it is also difficult to prepare such large quantities in a sufficiently pure condition. Stas' silver is considered to have contained impurity to the extent of 0·06 gram in the 400 grams used, so that there was no point in weighing to greater exactness than 0·06 gram. Actually silver is very difficult to obtain in a state of purity; de Gramont [1] states that silver when examined spectroscopically always contains traces of calcium, copper, gold, and magnesium and points out the importance of this in atomic weight determinations. Guye [2] in a series of papers on the errors which affect atomic weight determinations states that gaseous impurities are very difficult to remove from silver. Even after bubbling hydrogen through the molten liquid, certain gases, notably carbon monoxide, may be retained in sufficient amount to affect the atomic weight; the case is further complicated by the fact that these gases are not evenly distributed through the metal.

In the preparation of a pure solid, recrystallization is one of the most frequent operations and it is desirable to effect as complete a separation as possible of the pure solid from the mother liquor and the impurities which it contains. The process of centrifugal drainage of crystals developed at Harvard has been most effective in removing liquid adhering to the outside of the crystals. But in addition to this we have to consider the possibility of the formation of solid solutions or isomorphous mixtures and also inclusions within the crystal structure of some of the mother liquor. It is found that this can only be removed completely by fusion in a dry atmosphere, and even then any impurity in the included liquid will remain. The presence of similar elements, such as sodium in a potassium compound, does not produce nearly such a big error in the atomic weight as would do, for example, water or dust from the air of the laboratory. Thus the presence of 0·1 per cent of cobalt in nickel bromide because of the similarity of the atomic weights of the two metals would be negligible. The removal of water is carried out at Harvard with the aid of a very simple piece of apparatus; this consists of a quartz tube containing the boat with the substance to be dried fitting by a ground joint to a soft glass tube in which is the weighing-bottle; near the joint there is a depression in the glass tube just big enough to take the stopper of the weighing-bottle. The quartz tube is heated while any suitable gas is passed; when it is considered that the water has been removed, the temperature is reduced and the gas displaced by pure dry air. By means of a wire pushed through the narrow end of the quartz tube, the boat is pushed over the stopper into the bottle and finally the lid is pushed into the neck of the bottle, which can then be transferred to a desiccator to cool and be weighed at leisure.

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[1] *J. Chim. Phys.*, 1916, *14*, 336.

[2] *Ibid.*, 25, 55, 83, 195, and 204.

When it is not possible to fuse a substance in order to dry it, perhaps because of decomposition, the procedure is to dry it with the apparatus described under standard conditions. Then to take some of the substance so dried, decompose it, collect the water evolved with the aid of phosphorus pentoxide, and weigh it ; in some cases it is thus found that the water can be reduced to a constant but known amount for which allowance can be made.

Another source of impurity is the power which solids have of adsorbing substances from solution ; this is specially likely when substances are formed by precipitation. An example is the precipitation of silver chloride from solutions of sodium chloride and silver nitrate ; here it is well known that the silver chloride will adsorb sodium chloride, silver nitrate, and sodium nitrate according to the conditions under which the precipitation is carried out. The difficulty can be avoided in a qualitative precipitation by the use of very dilute solutions, but this could not be done in a quantitative precipitation because of the solubility of the silver chloride. In this case the amount of silver chloride remaining in solution has to be estimated. The solubility is decreased by the presence in the solution of an excess of either silver or chloride ions, so that an actual measurement is necessary, and for this purpose Richards developed the use of the nephelometer (*q.v.*). The physical form of a precipitate is also important ; large crystals are liable to contain more impurity than small ones ; a spongy precipitate is more readily washed pure than a crystalline one.

The material used in the vessels in which reactions are carried out is of great importance. Stas, who used glass vessels, was always troubled with silica derived from the glass. For accurate work quartz is satisfactory for acid solutions and platinum for alkaline.

In the quantitative drying of solids, attention must be given to the fact that the escape of gas from a solid is often accompanied by the removal of very fine particles of the solid itself : also in the evaporation of solutions when this is carried out by boiling, the bursting bubbles throw up small particles of spray containing some of the dissolved substance. Evaporation is therefore best carried out without boiling and may be accelerated by a down draught of pure air. The purification of gases used for this and similar operations is a matter for consideration, thus it is pointed out that it is often recommended to purify hydrogen by passing it in turn through permanganate, silver nitrate, concentrated sulphuric acid, and calcium chloride. The permanganate may add traces of oxygen, the action of light on the silver nitrate liberates oxides of nitrogen, the hydrogen reduces some of the sulphuric acid to sulphur dioxide and the calcium chloride may add some water so that the last state of the hydrogen is worse than its first.

It was stated above that in order to prevent adsorption on the precipitate it was advisable to work with very dilute solutions, but here again it must be remembered that a number of substances undergo hydrolysis with water.

Finally, it is to be desired that more attention should be given in the case of preparations supposedly pure to their spectroscopic examination as recommended by de Gramont.[1]

Approximate Methods for the Determination of the Atomic Weight

As stated above, the chemical method gives the combining weight or equivalent weight of the element and to get the atomic weight we require the further information as to what is the formula of the compound used or, what is the same thing, what is the valency of the element. Thus we may use the four steps:

1. Determination of the exact value of the combining weight.
2. Determination, by one of the methods described below, of the approximate equivalent weight.
3. From 1 and 2 find the valency.
4. From 1 and 3 find the exact value of the atomic weight.

To take an example from Richards and Baxter's value of the equivalent weight of iron, 18·6276.

Here we might use Dulong and Petit's generalization that the atomic weight multiplied by the specific heat is equal to 6·2. If the specific heat of iron is 0·115 the atomic weight is 6·2/0·115 approximately and this is 54.

If the equivalent weight is 18·6 and the atomic weight approximately 54, the valency V is given by A.W. = E.W. × V and V = 54/18·6 = 2·9 approximately, and since the valency must be a whole number the valency is 3 exactly.

The exact value of the atomic weight is now 18·6276 × 3 = 55·8828. The approximate methods which help us to the value for the second step are:

1. Cannizzaro's method depending on finding the least weight of the element occurring in 1 gram molecular weight of any of its compounds.
2. Dulong and Petit's generalization.
3. The Periodic Classification.
4. Evidence based on Isomorphism.
5. Information derived from spectra.
6. Transparency to X-rays.
7. The ratio of the specific heats of gases.

Cannizzaro's Method. This depends on the definition that the atomic weight of an element is the least weight which ever occurs in the gram molecular weight of any of its compounds.

The method is of limited application because it is necessary that the element in question shall form a considerable number of gaseous compounds suitable for the determination of the molecular weight, making use of the definition that this is the weight which occupies a volume of 22·4 litres at N.T.P. The assumption is that if we examine a sufficient number of different molecules containing the element in question we are very likely to hit on one molecule at least which contains only one atom of this element, in view of Dalton's statement that in general the atoms of the elements combine in small numbers. In fact, the method is limited to the non-metals since these alone give rise to the necessary gaseous compounds, and this is fortunate since it is just in the case of the non-metals that Dulong and Petit's method is of no value. The method requires the determination of the molecular weight and the analysis of each of the compounds and may be illustrated by reference to the case of nitrogen. In the following table are given the data successively; in column i the name of the compound; column ii the weight of 22·4 litres, i.e. the molecular weight; column iii the percentage of nitrogen in the compound found by analysis; column iv the weight of the nitrogen in 1 gram molecular weight.

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[1] *Loc. cit.*

Nitrous oxide . . .	44	64	28
Nitric oxide . . .	30	47	14
Ammonia	17	82	14
Nitric acid	63	22	14
Hydrazine	32	87	28

The figures given are only approximate, but this is all that is necessary and they show that in a gram molecule of no compound is there less than 14 grams of nitrogen: 14 is therefore the atomic weight of nitrogen.

Dulong and Petit's Generalization. This stated that for solid elements except non-metals of low atomic weight the product of the atomic weight and the specific heat is a constant, the value of which is 6·4.

Elements such as carbon and boron gave very low values for the product which can be called the atomic heat, and at one time attempts were made to fit them into the 'law' by showing that their specific heats and hence their atomic heats increase when the specific heat is determined at high temperatures. This, however, cannot be allowed because the specific heats of most elements increase with rise of temperature. It would be possible to find a temperature for each element at which it fitted the law, but this would make the method quite useless for determining the atomic weight, because we should not know what was the appropriate temperature for the determination of the specific heat of the particular element under consideration whose atomic weight was unknown.

In practice specific heats are usually determined over the range 100° — 20° C., and with the values so obtained Dulong and Petit's generalization is approximately correct, although the value of the constant is probably nearer 6·2 than 6·4. The law has been useful in the fixing of the atomic weights of iridium, cerium, lanthanum, and uranium.

The equivalent weight of uranium is 39·75: its atomic weight is therefore this number multiplied by the valency, which must be a whole number. Uranium was supposed to resemble iron and in this case the formula of the highest oxide would be U_2O_3 corresponding to ferric oxide Fe_2O_3. Mendelejeff, however, wished to place it in the sixth group of the Periodic system; a highest oxide UO_3 corresponding to the chromium oxide CrO_3 was then to be expected and a valency of six. The difficulty was solved when Zimmermann[1] found the specific heat of the element to be 0·027. This would give the approximate atomic weight 6·2/0·027 = 229 and the valency 5·6. The correct valency is thus 6 and not 3, and the atomic weight 238·5 instead of 119·25. Neumann [1] extended Dulong and Petit's work by showing that in certain groups of compounds the product of the molecular weight and specific heat is a constant. This is illustrated in the following table :

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[1] *Ber.*, 1882, *15*, 847.

Compound	M.W.	S.H.	M.W. × S.H.
$CaSO_4$	136	0·197	26·8
$SrSO_4$	185	0·143	26·3
$BaSO_4$	233	0·113	26·4
$PbSO_4$	303	0·087	26·4

Similar results were obtained with metallic halides, oxides, carbonates, &c.

Joule [2] and Woestyn [3] showed that the molecular heats of compounds could be considered to be the sum of the atomic heats of their constituents. The truth of this was established by Kopp [4] and is known as Kopp's Law. Attempts are sometimes made to show that the atomic heats of non-metals of low atomic weight as determined by Kopp's law agree with those determined by experiment. Friend [5] calculates the atomic heat of oxygen from the molecular heat of copper oxide to be 5·4 and compares this with the atomic heat calculated from the specific heat of liquid oxygen at -- 190° C., which gives the value 5·55. Such a comparison is not justified, first because the specific heat of liquid oxygen is used whereas the law refers to the specific heat of solids and secondly because the temperature of one determination was − 190° C. and that of the other presumably between 20° and 100° C. No useful purpose is served by these attempts to bring the non-metals of low atomic weight into line. Thus the oxides of copper, mercury, and nickel give an average value for the molecular heat of 11·5, hence the atomic heat of oxygen is 11·5 − 6·2 = 5·3.

The average molecular heat of the sulphides of iron, lead, and mercury is 12·0 and so the atomic heat of sulphur is 12·0 − 6·2 = 5·8.

Now the molecular heat of barium sulphate is 26·4 and if we subtract from this the atomic heat of one atom of sulphur and four atoms of oxygen we get the atomic heat of the barium—0·6. With a very simple compound, however, the method may be useful since if there are three atoms in the molecule the molecular heat will be near 18.

The Periodic Classification. The classical example of the value of this method is the case of the element beryllium. The equivalent weight is 4·55 and Berzelius,[6] on account of its resemblance to aluminium, considered it to be trivalent so that its atomic weight would be 13·65 and it would come between carbon (12) in group 4 and nitrogen (14) in group 5. There is no place for it here, while there is a place vacant between lithium (7) and boron (11): if beryllium were divalent its atomic weight would be 9·10 and it would fit into this position. We now know that this is the correct place for the element. Other cases in which the Periodic system led to the correction of inaccurate values of atomic weight are the cases of osmium, iridium, and platinum.

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[1] *Pogg. Annalen,* 1831, *23,* 1.

[2] *Phil. Mag.,* 1844, *25,* iii, 334.

[3] *Ann. Chim. Phys.,* 1848, *23,* iii, 295.

[4] *Proc. Roy. Soc.,* 1864, *13,* 229 ; *Phil. Trans.,* 1865, *155,* 71.

[5] *Text Book of Inorganic Chem., 1,* 96.

[6] *Schweigger's Journ. Chem. Pharm.,* 1816, *17,* 296.

Evidence based on Isomorphism. Mitscherlich studied the arsenates and phosphates of certain metals and from his results deduced the law that substances possessing an equal number of atoms united in the same manner exhibit complete identity of crystalline form.[1]

The law is not strictly true: substances which are regarded as isomorphous do show small differences, while substances like sodium nitrate and calcite which correspond very closely in crystalline form are not regarded as being isomorphous; again, groups such as ammonium can replace elements like sodium and potassium in isomorphous compounds.

The two criteria which are generally accepted as establishing isomorphism are the formation of mixed crystals and the formation of layer crystals. Some salts such as potassium sulphate and ammonium sulphate can yield single crystals which contain both salts and by varying the composition of the solution from which the crystals separate, crystals containing practically any ratio can be obtained; with other pairs of salts such as the chlorides of potassium and ammonium mixed crystals can be obtained, but only with a limited range of composition. The formation of layer crystals is very well shown by the alums, and if a coloured alum such as iron alum is chosen as the starting-point and this is grown in a saturated solution of potash alum the octahedron of iron alum can be seen very clearly within the octahedron of ordinary alum.

The way in which isomorphism can be useful in the determination of atomic weight is illustrated by the case of selenium.

Mitscherlich concluded that potassium sulphate and potassium selenate were isomorphous, and so if the formula of one is K_2SO_4 that of the other is K_2SeO_4. Now analysis shows that the selenate contains 35·8 per cent of selenium and 28·9 per cent of oxygen. SeO_4 contains 1 gram atom of selenium to 64 grams of oxygen so Se : 64 :: 35·8 : 28·9 hence

$$\mathrm{Se} = 64 \times 35{\cdot}8/28{\cdot}9 = 79{\cdot}2.$$

The law was actually used to correct the atomic weights of gallium and vanadium.

Information derived from Spectra.[2] Rydberg showed that a number of series of lines occur in the spectra of gases which can be represented by equations of the type $n = n_{\infty} - \mathrm{N}/(m + \mu)^2$ where N is the Rydberg constant 109675, m is an integer, and n and μ are two constants which are special for each series. In general, there are three associated series in each spectrum, the Principal (P), Diffuse (D), and Sharp (S) series. The equations for the three series may be written:

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[1] *Ann. Chim. Phys.*, 1820, *14*, 72; 1821, *19*, 350; 1924, *24*, 264.

[2] For full details of the use of the series lines in spectra the reader is referred to Baly's *Spectroscopy* (Longmans) and for a good summary to Friend's *Text Book of Inorganic Chemistry*, *1*, 234.

$$\begin{aligned} \mathrm{P}: &\ n = \mathrm{P}_\infty - \mathrm{N}/(m+p)^2 \text{ where } m \text{ is } 1, 2, 3, \&c., \\ \mathrm{D}: &\ n = \mathrm{D}_\infty - \mathrm{N}/(m+d)^2 \text{ where } m \text{ is } 2, 3, 4, \&c., \\ \mathrm{S}: &\ n = \mathrm{S}_\infty - \mathrm{N}/(m+s)^2 \text{ where } m \text{ is } 2, 3, 4, \&c. \end{aligned}$$

The series are connected by a number of relationships such as:

$$\begin{aligned} &(a)\ \mathrm{D}_\infty = \mathrm{S}_\infty \\ &(b)\ \mathrm{P}_\infty - D_\infty = \mathrm{P}(1) \\ &(c)\ \mathrm{S}(1) = -\mathrm{P}(1) \end{aligned}$$

When each component of a series is a doublet in the P series each doublet series may be taken to be made up of two single-line series converging to the same limit. The intervals of successive doublets converge to zero as m increases in a P series, but in the D + S series the interval is constant and equal to the first interval in the P series. In triplet series similar relationships hold in the P, D, and S series.

In a triplet the intervals are denoted by V_1 and V_2, V_1 being the interval between the middle and the least refrangible line and V_2 that between the most refrangible and middle line. In the D and S series these intervals are constant and equal to the intervals for the first P triplet.

Rydberg found that in the spectra of analogous elements the intervals of the doublets or triplets of the D and S (or P_1) were nearly proportional to the squares of the atomic weights of the elements; thus for cadmium and zinc

$$\begin{aligned} (V_1 + V_2)_{\mathrm{Cd}}/(V_1 + V_2)_{\mathrm{Zn}} &= 2{\cdot}948 \\ \mathrm{Cd}^2/Zn^2 &= 2{\cdot}960 \end{aligned}$$

Runge and Precht [1] compared the spectrum of radium with those of magnesium, calcium, strontium and barium and obtained the value of the atomic weight of radium to be 257·8 (instead of 226). The method is therefore inexact.

An empirical equation connecting the logarithm of the atomic weights and the frequency intervals has the form

$$\text{Log A.W.} = a + b\,(\log \mathrm{V}) + c\,(\log \mathrm{V})^2 + \ldots$$

Interpolation in such equations gives good results for the atomic weight and even extrapolation enabled Watts[2] to obtain the value 226·6 for radium.

Lecoq de Boisbaudran used spectra in the calculation of the atomic weights of gallium and germanium.

Transparency to X-rays. Benoist [3] noted that the stopping-power of the elements for X-rays was simply related to the atomic weight of the element. The intensity I of the rays passing through a layer of the element of thickness t is given by

$$\mathrm{I} = \mathrm{I}_0 e^{-kt}$$

where k is a constant the value of which depends on the element used. The stopping-power is found to be an additive quantity so that the stopping-power of a compound is the sum of the stopping-power of its constituent elements. It is thus possible to make an estimate of the atomic weight of an element which has not been isolated. So Benoist was able to show that the atomic weight of indium was 113·4 instead of 75·6. The atomic weights of thorium and cerium were fixed at 232 and 140·25 respectively and the value 9·1 confirmed for beryllium.

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[1] *Phil. Mag.*, 1903, *5* (VI), 476.

[2] *Ibid.*, 1904, *8* (VI), 279; 1909 (VI), 411.

[3] *Compt. rend.*, 1901, *132*, 324 and 545.

The Ratio of the Two Specific Heats of a Gas. When a gram molecule of a gas has its temperature raised by 1° C. the equation $PV = RT$ shows that the external work done is equal to R. It can be shown that the translational energy of the molecules of the gas is given by $3R/2$. Therefore if there are no other energy changes involved, the specific heat at constant pressure being denoted by C_p and that at constant volume by C_v,

$$\frac{C_p}{C_v} = \frac{R + 3R/2}{R} = 1{\cdot}67$$

The ratio $\frac{C_p}{C_v}$ is denoted by the symbol γ and it is found that with gases which are known to be monatomic $\gamma = 1{\cdot}67$.

With diatomic molecules rotational energy is possessed as well as translational and if the temperature is raised energy will be used up in increasing this rotational energy : if this increase in energy is denoted by E (for 1 gram molecule and 1° C. rise) γ becomes $\frac{5 + E}{3 + E}$ and this must be less than 1·67.

A triatomic molecule is capable of more complex rotation and so E might be expected to be greater and therefore γ still smaller.

The value of γ is found by measuring the velocity of sound in the gas by the Kundt's tube method (*q.v.*) and substitution in the equation

$$V = \sqrt{\frac{\gamma p}{d}}$$

where p is the pressure and d the density of the gas.

It is found by experiment that for diatomic gases the value of γ ranges from 1·41 for gases like oxygen and nitrogen down to 1·30 for easily liquefiable gases like chlorine. Triatomic molecules like CO_2 give values for γ less than 1·3.

The method has been particularly useful for the inert gases in Group O of the Periodic system. These give no compounds for the determination of the atomic weight by ordinary methods, but their molecular weights can be determined from their vapour densities. Their values for γ approximate closely to 1·67 so that they are monatomic and their atomic weights are identical with their molecular weights.

Example of Determination of Atomic Weight in Synthesis from Elements

The example given is the determination by Noyes and Weber[1] of the atomic weight of chlorine by direct combination with hydrogen. Noyes had previously determined the combining ratio of hydrogen and oxygen[2] and there was only one direct comparison of hydrogen and chlorine previous to the present work, that of Dixon and Edgar.[3] Richards had determined the ratio of silver to chlorine,[1] and silver and chlorine had then been much used in the atomic weights of other elements, the results being calculated to the oxygen standard using the ratio silver : oxygen : : 107·93 : 16. There was already a suspicion that this value for silver was too high so that it was very desirable to bridge the gap between Richards' Ag : Cl ratio and Noyes' H : O ratio by a determination of the ratio Cl : H.

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[1] *Bulletin of the Bureau of Standards*, *4*, No. 3.

[2] *Ibid.*, *4*, 173.

[3] *Phil. Trans.*, *A.*, *205*, 169.

Noyes' Method. The hydrogen was weighed while adsorbed on palladium (note the advantage of the small volume), the chlorine was weighed in the form of potassium chloroplatinate and the hydrogen was then released from the palladium by heating, to be passed over the heated chloroplatinate, whereby hydrochloric acid was formed which was absorbed in water and weighed. Since the weights of hydrogen, chlorine, and hydrochloric acid were obtained, two series of independent ratios were obtained and a double check on the results obtained.

Purification of Materials

The **hydrogen** was obtained in the first series by the electrolysis of sulphuric acid and in the second series by the electrolysis of barium hydroxide.

Platinum. The metal in the form of sponge was dissolved in *aqua regia* and evaporated to expel nitric acid ; the other platinum metals were removed by Schneider and Schubert's method.[2] The chloroplatinic acid solution was made alkaline with sodium hydroxide, boiled for half an hour, acidified and converted to potassium chloroplatinate. This was then reduced to platinum black by means of sodium formate. The platinum black was heated with dilute hydrochloric acid to remove iron and then washed until it began to pass through the filter as colloidal platinum. It was then redissolved and the process repeated until the mother liquors from the chloroplatinate precipitation were practically colourless and free from other platinum metals.

Potassium Chloroplatinate. The solution of the purified platinum in *aqua regia* was found to be unsatisfactory. It was difficult completely to remove nitric acid and the final product would not stand heating to 400° C. as did that obtained by the method used, which was to dissolve the platinum electrolytically in purified hydrochloric acid. The solution so obtained containing 120 grams of platinum in 500 ml. was evaporated to half its volume in a glass-stoppered wash-bottle while a current of chlorine was passed through the boiling solution. The chlorine was prepared by acting on pure potassium permanganate with pure hydrochloric acid which had previously been boiled with a little permanganate to remove any traces of bromine. The solution contained an excess of 100 grams of hydrochloric acid, and after filtering and diluting to 1 litre was precipitated by 1 litre of a solution of potassium chloride containing 33 per cent more than the theoretical requirement. The excess of hydrochloric acid and of potassium chloride were to check hydrolytic decomposition and this was also the reason for precipitating from concentrated solutions. The platinum solution was poured in a fine stream into the potassium chloride solution with air stirring, up to 4 hours being taken for the precipitation of 300 grams of the chloroplatinate. The precipitate so obtained was microcrystalline and pale yellow. It was filtered on a hardened filter with the aid of suction and washed with water, alcohol and ether. After removal to a platinum dish it was heated on an electric air-bath to drive off most of the remaining water and the quantity for a single determination transferred to a hard glass tube which was heated in a cylindrical air-bath to 400° C., while a current of air dried with sulphuric acid and phosphorus pentoxide was passed over it. The temperature was raised gradually and heating continued until no more hydrochloric acid was given off; this took 7 hours or more. The chloroplatinate was then transferred to the reaction apparatus with as little exposure to air as possible through an opening which was then sealed off; it received a final drying by heating and evacuation in this apparatus.

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[1] *J. Amer. Chem. Soc.*, 1905, *27*, 459.

[2] Graham Otto's *Lehrbuch*, 5th ed., *4*, 1153.

Potassium Chloride. The pure commercial salt was recrystallized from a solution made alkaline with potassium hydroxide in order to remove ammonia. It was redissolved and chlorine passed through the hot solution for several hours in order to remove traces of bromine. The salt was then recrystallized five times from water and precipitated three times by hydrochloric acid. Centrifugal drainage of the crystals was used. It was found by testing that the crystals contained less than one part of bromine in 50,000.

Hydrochloric Acid. The pure acid used was found to be free from sulphuric and nitric acids. Chlorine was passed through it for one day and then air was bubbled through till all the chlorine was removed: this required about 12 hours.

Chlorine. All the chlorine used was made from pure potassium permanganate and hydrochloric acid which had been previously boiled with a little permanganate.

Water. Distilled water was redistilled from alkaline permanganate, rejecting the first part of the distillate until it no longer contained ammonia.

Weighings. The air in the balance case was dried by a current of air. Each piece of apparatus was weighed with a counterpoise approaching it within 1 ml. in volume and 30 grams in weight. In the case of hydrogen the counterpoise was within 0·3 ml. of the volume and 2 grams of the weight. After a determination all pieces of apparatus and their counterpoises were rinsed with distilled water and wiped dry. They were next suspended in a desiccator through which a current of dry air was passed and were then transferred to the balance case. 12 to 24 hours was in some cases necessary to attain constant surface conditions. The air current in the balance was stopped 20 minutes before a weighing was made and duplicate weighings made at intervals of an hour or more rarely differed by more than 0·05 mg.

Method of carrying out a Determination

First Series. The apparatus was made in three parts: (I) the palladium tube, (II) the chloroplatinate tube, and (III) the apparatus for absorption of the hydrochloric acid. Each tube was fitted with taps and joints by which the pieces could be sealed together with Khotinsky cement. Pieces I and II were not joined directly but by a U-tube to which was attached a manometer and a connexion to the pump. The apparatus is shown diagrammatically in Fig. 1 (III^3).

The Palladium Tube was shaped as shown: the tube on the right is bent down and tapered so that it will fit into the socket of the U-tube as shown at B or into a similar socket on a tube attached to the hydrogen generator. This joint like all others was made with Khotinsky cement. The connexion to the hydrogen generator having been made, the three-way tap nearby was turned so that the air in the short piece of tube was expelled and then turned so that the gas entered the palladium tube. When no more hydrogen was adsorbed, the tap at A was opened for a short time and gas allowed to sweep through. The stop-cocks were then closed and after cleaning the apparatus was ready for weighing. The first time the tube was used, it was repeatedly charged with hydrogen and the hydrogen driven out at 400° C. In succeeding experiments the tube was ready for charging anew after each experiment.

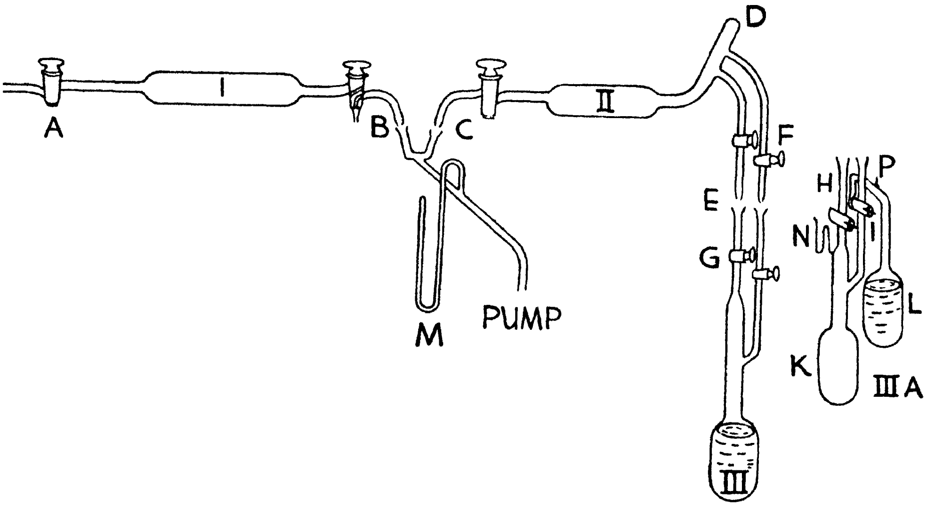

FIG. 1 (III^3)
I. Palladium tube
II. Chloroplatinate tube
III and IIIA. Absorption apparatus

The Chloroplatinate Tube. The chloroplatinate was introduced at D by connecting to this by means of a short piece of stout rubber tubing the hard glass tube in which the chloroplatinate had been heated to 400° C.; on shaking, the salt passed into the tube and D was sealed without allowing the flame gases to enter the tube. The apparatus was then evacuated with a Sprengel pump to a few thousandths of a millimetre of mercury while the temperature was maintained at 350° C. for 4 hours. The stop-cock was closed, and after cooling this piece of apparatus was ready for the preliminary treatment before weighing.

The Absorption Tube for Hydrochloric Acid has a bulb as shown with a volume of 100 ml.; 50 ml. of boiled distilled water were placed therein and it was evacuated with the pump, which in this case was protected by an extra phosphorus pentoxide tube. The evacuation was continued till no more air could be removed from the apparatus and the liquid. It was generally found necessary to allow the partly evacuated apparatus to stand for a day before the last traces of air could be removed from the water. This apparatus was now ready for washing and weighing. After weighing, the apparatus was set up as shown in the diagram and pieces I and II were each enclosed in an electric heater. The chloroplatinate in II was raised to 300° C., and connexion was made to the pump so that the air in B and C was removed, the taps at C and F were then opened so that the air in the tubes at E was withdrawn over the chloroplatinate. The evacuation was continued until the McLeod gauge showed the pressure to be only a few thousandths of a millimetre of mercury. The connexion with the pump was now cut off and tap B opened and the gradual heating of the palladium tube commenced. Then stop-cock C was opened very gradually and the hydrogen admitted to the chloroplatinate. The four cocks connecting pieces II and III had next to be opened, also very gradually, since a sudden inrush of gas would carry over very fine particles of the chloroplatinate. The taps joining the lower tube in D were first opened and then those to the upper tube. The reason for the two tubes is that some hydrogen is carried over with the hydrochloric acid and since it would not be absorbed by the water it would accumulate in a single tube and cause a lock, while with the two tubes as shown the light gas hydrogen will tend to pass up the right-hand tube and so go back to the chloroplatinate. The temperature of the palladium tube was now raised through a period of several hours, the gas pressure in the apparatus always being maintained at or just below one atmosphere. This pressure could be read by means of the small mercury manometer shown at M. The closed end contained a little air and with it pressures could be read from zero to one atmosphere, although its length did not exceed 10 cm.

When it was considered that enough hydrogen had been evolved, the tap B was closed and the palladium was allowed to cool. The temperature of the chloroplatinate tube was allowed to rise to 350° C. and the absorption tube, which up to this time had been kept at 0° C., was now cooled to – 20° C. by a mixture of ice and dilute sulphuric acid. The manometer showed that the conversion of the hydrogen remaining in contact with chloroplatinate into hydrochloric acid and the absorption of this by the water continued for 2 or 3 hours, by which time the manometer was at the lowest point which it could indicate. The stop-cocks connecting pieces II and III were now closed. The gas in II was pumped out and analysed, volumes being read at a pressure of one-sixth of an atmosphere : under these conditions 1 ml. of hydrogen would weigh less than 0·02 mg.

The apparatus was now dismantled and the parts cleaned and prepared for weighing. The parts were left in the desiccator overnight and weighed the next day.

The Second Series of Experiments will not be described in detail; the main differences were two : firstly, the hydrogen was generated from barium hydroxide, and secondly the apparatus for the absorption of the hydrochloric acid was modified (IIIA) so that the acid was first condensed to liquid by means of liquid air and connexion to the bulb containing the water was not made until connexion with the chloroplatinate had been closed so that there could be no possibility of water getting back into piece II. (See original paper.)

Errors and Corrections are discussed in the original paper. Hydrogen remaining in the chloroplatinate tube was withdrawn with the gases which were analysed at the end of the determination : the average amount was 0·047 mg. In some cases, when the stream of hydrogen was too slow, a little hydrochloric acid found its way into the palladium tube when this tube was refilled with hydrogen for a new experiment, the presence of the acid was tested for by passing some hydrogen through the tube into water coloured with a drop of methyl orange : if any acid was found, all the hydrogen was driven out of the palladium through the water and the amount of acid determined with standard alkali : when the correction was necessary the value varied between 0·35 and 9·26 mg.

The freedom of the chlorine from bromine was judged to be sufficient, since the amount of this was less than 1 in 50,000 which would not introduce an error greater than 1 in 100,000. The presence of volatile products in the platinum or of elements which could produce such compounds as ammonia seems to be precluded by the methods of preparation used and the heating of the chloroplatinate to 400° C. for a protracted time. It is known that the chloroplatinate hydrolyses in aqueous solution so that the presence of water, hydroxyl or oxygen was a possibility. As already described, the salt was precipitated from concentrated solutions and always with an excess of potassium chloride and hydrochloric acid and was separated from the mother liquor as soon as possible. It was shown that all hydrochloric acid could be removed by heating to 400° C. and that the resulting salt was neutral : it can be presumed that any water was also lost. The agreement between the two series of experiments is also noteworthy : in the first, the chloroplatinate was in contact with water vapour during the experiments, while in the second series it was in equilibrium with solid hydrochloric acid at − 180° C. at which temperature this is a perfect drying agent. The difference in the two series is 1 in 10,000 while the presence of 0·05 per cent moisture on the salt would produce a change of about 17 in 10,000. Finally 100 gm. of chloroplatinate were completely reduced with hydrogen and the hydrochloric acid produced was made to pass through a U-tube at − 78° C. and then the apparatus was evacuated : the tube gained 0·9 mg. and this represents 1 in 30,000 of the weight of hydrochloric acid formed. As already stated, the amount of nitrogen or air left in the chloroplatinate tube at the end of an experiment was determined ; the correction for this was never more than 1 in 10,000.

Corrections were made to the gain in weight of the absorption tube for any acid found in the palladium tube and for that pumped out of the chloroplatinate tube : the last amounted from 1·27 mg. down to zero. In the second series in some of the experiments a little chloroplatinate was blown over ; this was determined and in three experiments the corrections were 2·03, 15·0 and 36·5 mg.

A final check is given by comparing the sum of the weights of hydrogen and chlorine used with the weight of hydrochloric acid formed.

The values obtained were:

1 No. of expt.	2 Hydrogen	3 Chlorine	4 Sum of 2 & 3	5 Hydrochloric Acid	6 A.W. of Cl.	M.W. of HCl
1 . . .	0·25394	8·93293	9·18687	9·18695	35·177	36·178
2 . . .	0·28004	9·85590	10·13594	10·13259	35·195	36·183
3 . . .	0·51821	18·23468	18·75289	18·75359	35·188	36·189
4 . . .	0·67631	23·79587	24·47218	24·47123	35·186	36·185
5 . . .	0·58225	20·48158	21·06383	—	35·177	—
6 . . .	0·47989	16·88423	17·36412	17·36310	35·184	36·182
7 . . .	0·64132	22·55816	23·19948	32·20054	35·175	36·176
Average of Series I: 35·183 and 36·181						
8 . . .	0·81608	28·71691	29·53299	29·53167	35·188	36·187
9 . . .	0·83194	29·28055	30·11249	30·11207	35·195	36·195
10 . . .	0·29074	13·74926	14·14000	14·14078	35·187	36·188
11 . . .	0·75560	26·58427	27·33987	27·33926	35·183	36·182
12 . . .	0·77518	27·26746	28·04264	28·04110	35·177	36·175
Average of Series II: 35·186 and 36·185						
Total average: 35·184(3) and 36·183(7)						

The value found for the atomic weight of chlorine is therefore 35·184 with a probable error of ± 0·0013. The value for the molecular weight of hydrochloric acid is 36·184 with a probable error of ± 0·0012. The combined values of both sections is 35·184 ± 0·0008.

The above figures all on the basis H = 1·000; changing to Noyes' value for the H : O ratio 1·00787 : 16 the value for chlorine becomes 35·452.

SECTION 2: THE METHOD OF LIMITING DENSITIES

Atomic Weight of a Gas. This method, first used by Guye and his school to get accurate results, has since been developed so that it has become one of the most precise methods for the determination of the molecular weight of a gas, and when the formula of the gas is known the atomic weight may be calculated. It is obvious that Avogadro's hypothesis cannot be correct for any pair of gases because these gases will show unequal deviations from the gas laws, so that if equal volumes of the two gases did contain equal numbers of molecules at one temperature and pressure, when these last were altered the volumes would alter to different extents and so would no longer be equal. The accuracy with which gases do obey the gas laws becomes the greater the lower the pressure; so it is desirable to compare the gases at as small a pressure as possible.

It has been found that the ratio of density to pressure is almost a linear function of the pressure, so that it is possible to extrapolate to zero pressure or at any rate to a very low pressure when it may be assumed that the gas behaves as an ideal gas. This is particularly true of gases which are difficult to liquefy. With other gases, it is necessary to carry out determinations at as low pressures as possible and carry out a graphic extrapolation. An example of the method will help to make it clear and some data obtained for carbon dioxide by Dietrichson, Miller, and Whitcher[1] are given in the following table:

DENSITY OF CARBON DIOXIDE AT 0° C.

Pressure in atm.	Density : grams per litre	Ratio d/p
1	1·976757	1·976757
$\frac{2}{3}$	1·314850	1·97228
$\frac{1}{2}$	0·985047	1·97009
$\frac{1}{3}$	0·655957	1·96787
$\frac{1}{4}$	0·491691	1·96676
$\frac{1}{6}$	0·327609	1·96565
0		1·96346

When d/p is plotted against pressure it is found that at zero pressure the value of d/p is 1·96346.

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[1] *J. Amer. Chem. Soc.*, 1941.

Similar data for oxygen are given by Baxter and Starkweather.[1]

DENSITY OF OXYGEN AT 0° C.

Pressure in atm.	Density : grams per litre	Ratio d/p
1	1·42896	1·42896
$\frac{3}{4}$	1·07149	1·42865
$\frac{1}{2}$	0·71415	1·42830
$\frac{1}{4}$	0·35699	1·42796
0	—	1·42767

Now according to Avogadro's law, the ratio of these limiting densities is the ratio of their molecular weights and since, by definition, the molecular weight of oxygen is 32, that of carbon dioxide is 32(1·96346/1·42767) and this is 44·010. Then if the formula of the gas is CO_2, the atomic weight of carbon is 12·010.

The method has been particularly useful with members of the Helium family where the chemical methods cannot be used. It is established by measurements of the velocity of sound in the gases that they are mon-atomic. Baxter and Starkweather[2] found that for neon and argon the values of d/p at 0° C. are 0·90043 and 1·78204, so that the molecular weights and the atomic weights are 20·183 for neon and 39·944 for argon.

Woodhead and Whytlaw-Gray[3] compare the pressures at which two gases have the same density ; this pressure ratio is determined at a number of pressures and the results are extrapolated to zero pressure.

Thus when oxygen pressures at 20° C. were $\frac{3}{4}$, $\frac{1}{2}$, and $\frac{1}{4}$ atmospheres, the ratio of this pressure to that of carbon monoxide having exactly the same density was respectively 0·87500, 0·87514, and 0·87523 and the extrapolated value for zero pressure was 0·87535. This gives the molecular weight of carbon monoxide $32 \times 0{\cdot}87535 = 28{\cdot}011$, and so the atomic weight of carbon is 12·011. For the determination of density two methods have been used—Regnault's,[4] and the volumeter method.

The globe method has been used by Morley,[5] Rayleigh,[6] Gray,[7] and Baume.[8]

A glass globe of known capacity is carefully cleaned, dried, evacuated, and weighed. It is then filled with pure gas at pressure p, and temperature t, this generally being the temperature of melting ice.

For the method it is not necessary to use very large globes. Rayleigh used a globe of volume 1·8 litres, while Guye, in his work on nitric oxide, used globes as small as 0·380 litre.

The use of small containing vessels might be expected to increase the errors due to adsorption on the surface of the glass since the proportion of surface area to volume is greater in small vessels. Attempts have been made[9] to measure this effect by determining the density of the same gas in bulbs of different sizes; if the effect is noteworthy the apparent density would be expected to be greater in the small bulbs; the results were, however, inconclusive, and only indicate that the effect is a small one.

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[1] *Proc. Nat. Acad. Sci.*, 1928, *14*, 50.

[2] *Loc. cit.*

[3] *J. Chem. Soc.*, 1933, 846.

[4] *Compt. rend.*, 1845, *20*, 975.

[5] *Zeits. physik. Chem.*, 1896, *20*, 1.

[6] *Proc. Roy. Soc.*, 1893, *53*, 134.

[7] *Trans. Chem. Soc.*, 1905, *87*, 1601.

[8] *J. Chim. Phys.*, 1908, *6*, 1.

[9] See Guye and Davila, *Mem. Sci. phys. nat.*, 1908, *35*, 635.

Small flasks have the advantage that the correction for the contraction of the flask on evacuation is proportionally smaller than for large flasks. This contraction is measurable by the method suggested by Travers.[1] The flask is supported inside a large desiccator which has two holes through the stopper in the lid. Through one of these holes passes the stem of the globe and through the other a calibrated capillary tube. The desiccator is filled with water up to a mark on the capillary and is immersed in a thermostat: the globe is then evacuated and the contraction obtained from the movement of the water in the capillary.

In the weighings the globe is always counterpoised with a similar globe made of the same kind of glass and having as nearly as possible the same external volume. The surfaces of the globe and its counterpoise are always treated in exactly the same way and thus difficulties due to the hygroscopic nature of the glass surfaces and to changes in the temperature and pressure of the air are eliminated as far as possible. Great care has to be taken that the inside of the globe is perfectly dry. This is ensured by filling it with air dried with phosphorus pentoxide and then evacuating, the process being repeated several times. Similarly, the evacuated flask is filled with the dry experimental gas and evacuated several times before the determination is made.

As an example of the method of calculation take the case of a gas at 0° C. and a pressure p approximately equal to 760 mm. of mercury. Let the empty globe exceed the tare by W_1 gram and the filled globe exceed the tare by W_2 gram. $W_2 - W_1$ is then the approximate mass of gas.

If the contraction due to evacuation is found by experiment to be e and the mass of 1 ml. of air under the conditions of experiment is a gram, the corrected mass of gas is $W_2 - W_1 + ae$ gram. If W grams of water fill the globe at 0° C. and d is the density of water at this temperature, the volume of the gas is W/d ml. or V litres. Then assuming the gas to obey Boyle's Law and the mass of 1 litre at N.T.P. being denoted by L,

$$L = \frac{760}{pV}(W_2 - W_1 + ae)$$

In order to convert this to the mass of a 'normal litre', i.e. measured at 0° C. and 760 mm. of mercury pressure at sea level in latitude 45°, the value of L must be divided by

$$(1 - 0{\cdot}0026 \cos 2\lambda - 0{\cdot}000000196h)$$

where λ is the latitude and h is the height in metres above sea level.

The volumetric method does not give better results than the globe method and will not be described. The reader is referred to Morley,[2] Gray and Burt,[3] and Perman and Davies.[4]

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[1] *Experimental Study of Gases*, Macmillan, 1901, 119.

[2] *Smithsonian Contrib.*, 1895, *29*.

[3] *Trans. Chem. Soc.*, 1909, *95*, 1633.

[4] *Proc. Roy. Soc.*, *A*, 1906, *78*, 28.

CHAPTER IV [3]

THE MASS SPECTROGRAPH

SECTION 1: METHODS OF WORKING

THE Mass Spectra of the elements have now been practically all examined, due largely to the brilliant researches of F. W. Aston. He has given an excellent and complete account of the subject in *Mass Spectra and Isotopes.*[1] This text must be consulted by anyone interested in this subject.[2] A brief outline only of the development of this subject will be recorded here, with references to the literature. A technical application of the mass spectrometer will be considered in Section 2.

Positive Rays. Goldstein in 1886 first observed these rays as streamers of light behind a perforated cathode when an electrical discharge was passed through gases at low pressures and he called them 'canal strahlen'.

The rays were fully investigated by J. J. Thomson who called them positive rays. They are produced by ionization by means of a strong electric field in gases under low pressure; the ionization which is due either to collision or radiation causes the separation of an electron from the atom leaving the residue positively charged. If the field is strong and the pressure is low so that the particle does not collide with others, it will be impelled with a high velocity in a direction opposite to that of the electron and becomes a positive ray. Molecules as well as atoms may become positively charged in the same way.

Methods of Detection. When the rays fall on a screen covered with powdered willemite they cause this to show a green glow at the point of impact: they affect a photographic plate and also can be made to fall on to a metal plate connected to an electroscope.

J. J. Thomson's Parabola Method of Analysis

J. J. Thomson showed that if a charged particle passes between two electrostatically charged plates it will be deflected towards the positive plate so that the point of impact on the screen moves a distance x. If the deflection is through a small angle $x = k\left(\frac{Xe}{mv^2}\right)$ where e is the charge, m the mass, and v the velocity of the particle and X is the strength of the field. If the electrostatic field is replaced by a magnetic field of strength H, the particle will be again deflected but now in a direction at right angles to the former one and will strike the target at a distance y from the point at which it would hit in the absence of the field: y is given by k' (He/mv). The constants k and k' depend on the dimensions and form of the apparatus; e is also a constant, equal to the charge on an electron 4·80 × 10^{-10} C.G.S. units or a simple multiple of this. If both fields are applied at the same time the particle will hit the screen at a point whose co-ordinates are x, y, and y/x is a measure of the velocity of the particle and y^2/x is a measure of e/m, the ratio of the charge to the mass of the particle. Therefore if we are dealing with a beam of positive rays all having the same mass but with varying velocities the locus of their points of impact will be a parabola. If the beam contains a second set of rays having a constant but larger mass m', these will give a second parabola but having a smaller magnetic displacement than the first. If now the direction of the magnetic field is changed a second pair of parabolas will be obtained which is the mirror image of the first in the OX axis. If now a line be drawn parallel to the OY axis and cutting the first parabola and its mirror image in p and r and the second one and its image in q and s, then $m/m' = (pr)^2/(qs)^2$. The apparatus used for obtaining the parabolas is shown in Fig. 1 (IV³).

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[1] The authors are indebted to the late Dr. F. W. Aston and Messrs. Edward Arnold & Co. for information obtained from *Mass Spectra and Isotopes*, as well as for permission to use diagrams given in this section from the book.

[2] Published by Messrs. Edward Arnold & Co., London, 2nd ed., 1942.

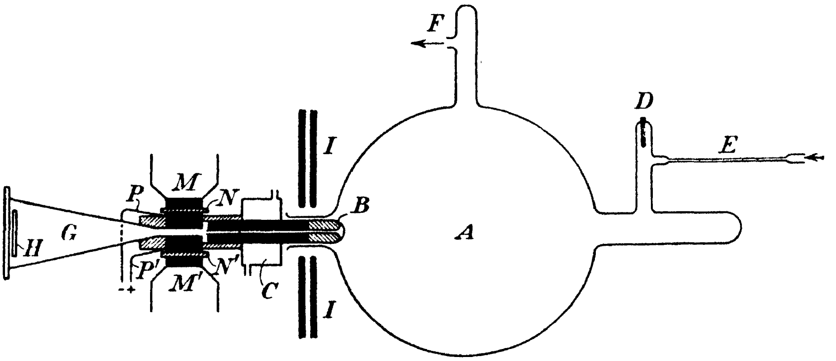

FIG. 1 (IV³)
Positive ray apparatus

A is a bulb of about 1½ litres like an X-ray bulb and having the aluminium anode D in a side-tube. The cathode is shown at B; it presents a hemispherical front to the tube and has a funnel-shaped opening in the centre continuing as a very fine bore tube of brass about 7 cm. long fixed in a thick iron tube which forms the continuation of the cathode which is cooled by the water jacket C. The finer the bore of the tube the more accurate the results, but the intensity falls off very rapidly so that the practical limit is 0·1 mm. P and P′ are the pole-pieces of the electromagnet MM′; they are insulated from this by the mica plates shown at NN′ so that the pole-pieces can be electrostatically charged by means of the leads shown. G is the highly exhausted camera chamber with the fluorescent screen or the photographic plate at H. II′ are soft iron screens placed between the electromagnet and the bulb to screen this from the magnetic field. At E is a very fine glass capillary through which gas from a gas holder is allowed to leak into A, from which it is pumped off at F by means of a Gaede rotating mercury pump. By alterations in the speed of the pump and the pressure of the gas in the holder the pressure in A may be kept at any desired value for a considerable length of time and is kept at such a value that the tube will operate at 30 to 50 kilovolts. Under these conditions positive rays are produced in A and under the high potential gradient move at high speeds towards the cathode, and those which are travelling in the line of the axis of the capillary tube will pass down it and straight on to the target if no electrostatic and magnetic fields are applied ; in the presence of these they will be deflected as explained above, the most rapidly moving particles, that is those which have been longest in the electrical field, being those which are least deflected and form the fairly sharp starting-point of the parabola.

The parabola method gave most valuable results in the early days and first indicated the existence of the two isotopes of neon, but it was not powerful enough to enable chlorine to be separated into its isotopes so that it became most important to work out an improved method to give more accurate results. This was done by Aston in 1919, who in that year commenced the design of the first mass spectrograph which was later improved to the final third form. These are completely described in Aston's *Mass Spectra and Isotopes.*[1]

The Mass Spectrograph

In the parabola method, many rays are lost by collision in the narrow canal-ray tube, very fine copper or brass tubes had their surfaces corroded by the impact of the rays so that they silted up, the total energy available for photography falls off as the fourth power of the radius of the capillary and the patches thrown on the screen are surrounded by a penumbra. Instead of the capillary of brass or copper, two fine apertures in aluminium were used, since this metal was found to be much more resistant to corrosion, and a very high vacuum was maintained between the two apertures by means of a subsidiary charcoal tube or pump. The introduction of two straight parallel slits to select the rays aimed at one particular part of the plate eliminates the difficulty of the penumbra and finally a method of focusing was devised.

Simplified Theory of Focusing

The rays after arriving at the cathode face pass through two very narrow slits of special construction S_1S_2, (Fig. 2 (IV^3)) and the resulting thin ribbon is spread out into an electric spectrum by means of the parallel plates P_1P_2. After emerging from the electric field the rays may be taken, to a first order approximation, as radiating from a virtual source Z half-way through the field on the line S_1S_2. A group of these rays is now selected by means of the diaphragm D and allowed to pass through the parallel poles of an electromagnet. For simplicity the poles are taken as circular, the field between them as uniform and of such sign as to bend the rays in the opposite direction to the foregoing electric field. Let X denote the strength of the electric field and θ the angle through which this deviates the rays and let H be the strength of the magnetic field and φ the deviation it produces. Then if l and L are the lengths of the paths of the rays in the electric and magnetic fields, the respective radii of curvature of the paths are, where θ is small, approximately l/θ and L/φ while the corresponding accelerations are

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[1] *Loc cit.*

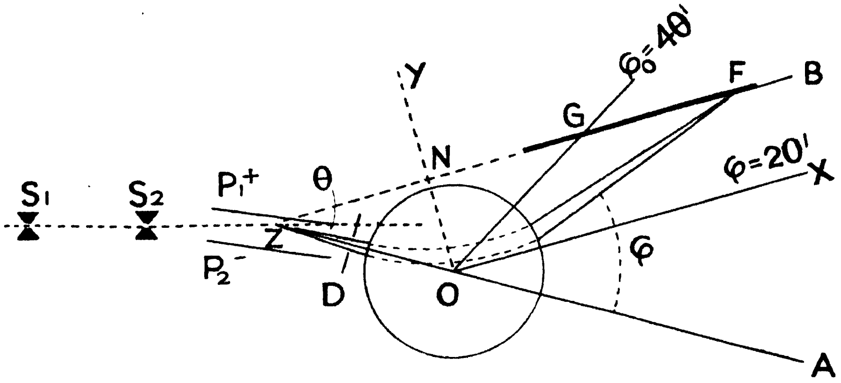

FIG. 2 (IV³)
Mass spectrograph—diagram

$v^2\theta/l$ and $v^2\varphi/L$, when v is the velocity of the beam. Hence, c being the electromagnetic constant and e and m the charge and the mass of the particles, we have

$$v^2\theta/l = eX/m$$

and

$$v^2\varphi/L = eHv/mc$$

Consequently over the small range of θ selected by the diaphragm, $v^2\theta$ and $v\varphi$ are constant for all rays of the same l/m. For variations of v we have

$$d\theta/\theta + 2dv/v = d\varphi/\varphi + dv/v = 0$$

so that

$$d\theta/\theta = 2d\varphi/\varphi$$

The rays emerging from the electric field may to a first order of approximation be taken as diverging from a source Z half-way through the field on the line S_1S_2, and if b be the distance from Z to O, the centre of the circular magnetic poles, the breadth of the beam of rays at O will be $bd\theta$. At a further distance r from O, the breadth will be $bd\theta + r(d\theta + d\varphi)$; using the above relation for $d\varphi$ this breadth is $d\theta[b + r(1 + \varphi/2\theta)]$, so that the beam comes to a focus when this expression is zero, or writing $\theta' = -\theta$, provided that $\varphi > 2\theta'$ when $r(\varphi - 2\theta') = 2b\theta'$.

Taking as axes OX and OY lines making angles with ZO through O equal to $Z\theta'$ and $\frac{\Pi}{2} + 2\theta'$ the focus F has co-ordinates $r \sin(\varphi - 2\theta')]$, or θ' and φ being small, approximately $[r, r(\varphi - 2\theta')$, which is $[r, 2b\theta']$.

Hence whatever the fields, provided that the diaphragm remains fixed, the foci will all lie on the straight line parallel to the x axis, whose equation is $y = 2b\theta'$, and which pass through the point Z. The thick line GF, G being the image of Z in OY, represents a photographic plate which will be in fair focus for a sufficiently large range of l/m. By control of the values of X and H any desired range of the spectrum may be brought on the plate. Fig. 3 (IV³) shows diagrammatically the original arrangement of the mass spectrograph when used for analysing positive rays generated by the ordinary discharge tube method.

The discharge tube B is an ordinary X-ray bulb 20 cm. in diameter. The anode A is of aluminium wire surrounded concentrically by an insulated aluminium tube to protect the glass walls, as in the Lodge valve.

The aluminium cathode C, 2·5 cm. wide, is concave, and placed just in the neck of the bulb—this shape and position having been adopted after a short preliminary research. In order to protect the opposite end of the bulb, which would be immediately melted by the very concentrated beam of cathode rays, a silica bulb D is mounted as indicated. The use of silica as an anti-cathode has the great advantage of cutting down the production of undesirable X-rays to a minimum. The cathode is earthed.

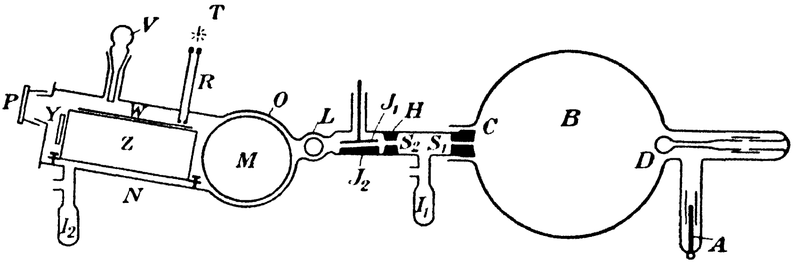

FIG. 3 (IV^3)
The first mass spectrograph

The discharge was maintained by means of a large induction coil actuated by a mercury coal-gas break; about 100 to 150 watts were passed through the primary, and the bulb arranged to take from 0·5 to 1 milliampere at potentials ranging from 20,000 to 50,000 volts. Owing to the particular shape and position of the electrodes, especially those of the anode, the bulb acts perfectly as its own rectifier. The method of mounting the cathode will readily be seen from Fig. 4 (IV^3), which shows part of the apparatus in greater detail. The neck of the bulb is ground off short and cemented with wax to the flat brass collar E which forms the mouth of the annular space between a wide outer tube F and the inner tube carrying the cathode. The concentric position of the neck is assured by three small ears of brass not shown. The wax joint was kept cool by circulating water through the copper pipe shown in section in Fig. 4 (IV^3). The gas to be analysed was admitted from the fine leak into the annular space and so to the discharge

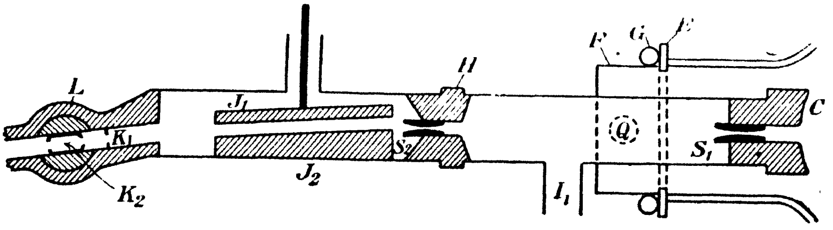

FIG. 4 (IV^3)
Mounting of cathode in the mass spectrograph

by means of the side-tube attached to F shown in dotted section at Q. Exhaustion was performed by a Gaede mercury pump through a similar tube on the opposite side. The reason for this arrangement is that the space behind the cathode is the only part of the discharge bulb in which the gas is not raised to an extremely high potential. If the inlet or outlet is anywhere in front of the cathode, failing special guards, the discharge is certain to strike to the pump or the gas reservoir. Such special guards have been made in the past by means of dummy cathodes in the base of the tubes, but, notwithstanding the fact that the gas can only reach the bulb by diffusion, this arrangement is far more satisfactory and has the additional advantage of enabling the bulb to be dismounted by breaking one joint only.

The Slit System. The very fine slits were made by boring a 1 mm. hole down the axis of an aluminium cylinder 10 mm. long and 5 mm. in diameter. The cylinder was then hammered till the circular hole became a slit 0·3 mm. wide. The central part of the cylinder was next placed between two V-shaped pieces of steel and crushed till the sides just touched : then by slight tapping at right angles the slit was slightly opened. In this way good slits could be made as fine as 0·01 mm. The hole was filled with hard wax and the outside turned up to a taper to fit the mounting. The two slits are adjusted parallel to each other by means of their diffraction patterns. The space between them was exhausted by means of the liquid-air-cooled charcoal tube I_1.

The Electric Field. The two flat parallel brass surfaces J_1 and J_2 are 5 cm. long and held 2·8 mm. apart by glass distance-pieces, the whole being wedged into the brass containing-tube. J_1 was raised to a potential of 200–500 volts by a battery of small storage cells. The plates were sloped at 1 in 20, i.e. half the angle of slope of the mean ray of that part of the spectrum to be selected by the diaphragms K_1 and K_2. K_1 is a rectangular hole in a brass plate fixed in the tube just in front of K_2, which is movable since it is mounted in the bore of the stop-cock L. K_1 stops any charged rays from striking any greasy part of the plug of the stop-cock. K_2 acts like two square apertures sliding past each other when the plug is turned, so that the angle of the rays can be stopped down to any desired extent by turning the plug, becoming zero before any greasy surface is exposed to the rays. The cock also serves to cut off the camera from the discharge tube, which is useful when changing plates.

The Magnetic Field. M shows the position of the pole-pieces of the Du Bois electromagnet of 2,500 turns. These pole-pieces have circular faces 8 cm. in diameter and are held 3 mm. apart by brass distance-pieces. The pole-pieces are cylinders and are soldered into the brass tube O which forms part of the camera N. The pole-pieces are fixed by screwed bolts into the arms of the heavy magnet which forms a very firm and rigid foundation for the whole apparatus. Soft iron plates are used to give magnetic shielding to the apparatus. The current is obtained from large accumulators. Magnetic saturation was obtained with about 5 amperes. With an E.S. field of 300 volts on the plates J this just brings the simply charged mercury lines into view; 0·2 ampere is enough to bring the hydrogen lines on to the scale.

The Camera. For details, Aston's work should be consulted, but we may say that the rays pass between the two vertical earthed brass plates 3 mm. apart connected at their tops to the horizontal brass plate X, in which there is a slit 11·8 cm. long by 2 mm. wide. On X rests the photographic plate and it can be moved horizontally over the slit to make an exposure by a mechanism operated through the ground glass joint V. I_2 is a charcoal tube for exhausting the camera.

Methods of Determining the Mass of a Particle

1. **Calibration with Known Lines.** None of the geometrical constants of the apparatus must be altered during the formation of the calibration curve and the determination of the unknown mass. A series of spectra are taken with for example a mixture of CO_2 and CH_4 in the tube: we should expect lines at 6 for C^{++}, 8 for O^{++}, 12 for C, 16 for O, 28 for CO, and 44 for CO_2: there will also be lines for CH, CH_2, and CH_3. These lines give a number of points on a calibration curve and enable the fiduciary point to be fixed. The gaps are filled up by means of a second spectrum of the same gases with a different magnetic field. If m_1, m_2, &c., were the known masses in the first case, the new distance can be converted by means of the curve into the new masses m'_1, m'_2, &c.,

$$\frac{m_1}{m'_1} = \frac{m_2}{m'_2}, \text{ \&c.} = r$$

so all average values of r can be obtained and the known masses m_1, m_2, &c., when multiplied by r give a new set of points on the curve.

2. **Method of Coincidence.** To compare an unknown mass m' with a known mass m. By altering the magnetic and electrostatic fields the line due to m' can be brought to any position on the plate and so to coincide with that of m. If X and H were the original fields and X′ and H′ the new ones,

$$\frac{m'}{m} = \frac{X}{X'} \times \left(\frac{H'}{H}\right)^2$$

In practice H, the strength of the magnetic field, is not easily measured, so H is kept constant and X alone varied: then $\frac{m'}{m} = \frac{X}{X'}$.

3. **Method of Bracketing.** This method was first used in the determination of the masses of hydrogen and helium which are far removed from the ordinary reference lines. The lines to be measured would be near to the geometrical progression 1, 2, 4, 8, &c. Two sets of accumulators each giving 250 volts were made to give exactly equal potentials by means of a subsidiary cell and a current divider. If the magnetic field was kept constant and two exposures were made, one with the two voltages on the E.S. field plate in parallel and the other with them in series the two sets would exactly overlap, but if we first add and then subtract a small voltage from the large potentials, using for example 250, 500 + 12 and 500 − 12 volts, two lines would be obtained which closely bracketed the first if the mass ratio was 2 to 1. This was found to be the case for the hydrogen molecule and the hydrogen atom but was not so for the helium molecule and the hydrogen

molecule, so it was possible to show that the mass of the helium molecule was less than twice that of the hydrogen molecule and led to the measurements of the 'packing fraction'.

Mass Rays of Metallic Elements

The gas discharge method already described can only be used for those elements which give gaseous or readily vaporizable compounds. Many metals are therefore excluded from this method. They may be examined by the 'Hot anode' method in which the anode is a platinum strip coated with a salt of the metal and heated electrically by means of a current supplied by an external battery. A second method consisted in the use of a composite anode using a mixed paste of graphite and the salt which was heated by the discharge itself.

Aston's second mass spectrograph was designed to increase the accuracy of the mass measurements so as to make it possible to measure the 'packing fractions'. It was set up in 1925 and had five times the resolving power of the earlier one, its accuracy approaching 1 in 10,000. This improvement was obtained by doubling the angles of electric and magnetic deflection and using slits placed farther apart, viz. 20 cm. instead of 10. The electric deflection was now one-sixth of a radian and the maximum voltage used was 400 volts from a specially built battery. For the magnetic deflection, sickle-shaped pole-pieces 3 mm. apart were used and the magnet was specially designed to give a constant field for long periods. In this apparatus the high vacuum necessary near the slit system was obtained with a high-speed mercury diffusion pump used in addition to the tubes containing charcoal cooled in liquid air. Polarization of the electric plates gave a great deal of trouble. It was partially overcome by heavily gilding them and partly by the method of measurement of the ratios of the field strengths.

The third mass spectrograph described in 1937 [1] had a scale which was closely linear: the dispersion coefficient for 1 per cent difference in mass was 3 mm. at one end of the plate and 6 mm. at the other. The microphotometer enabled the position of a line to be fixed to 0·005 mm. corresponding to one part in 100,000 in mass. In this apparatus the narrow slits were adjustable from outside by means of a ground glass joint so that their width could be varied from 0·05 mm. down to zero; the advantage of very narrow slits was unfortunately to some extent neutralized by their intense polarization by the beam.

In the new instrument an electric deflection of a quarter of a radian in a radial field of radius 40 cm. was used: this was followed by magnetic deflection by a uniform field between sickle-shaped pole-pieces which were sections of a circle 15 cm. in diameter since these dimensions were calculated to be favourable. The magnetic field was kept steady by a hand-operated spiral mercury resistance and a fluxmeter showing changes of one in 10^5 was used.

The electric plates were made removable for cleaning as an aid in reducing the polarization effect.

A diagram of this spectrograph is shown in Fig. 5 (IV^3).

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[1] *Proc. Roy. Soc., A.*, 1937, *163*, 391.

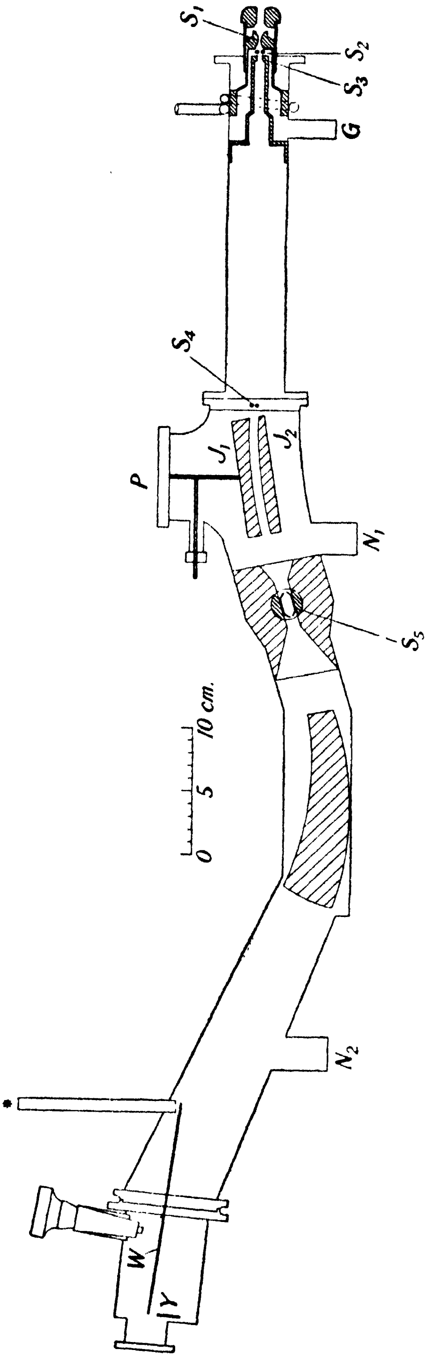

FIG. 5 (IV^3)
Aston's third mass spectrograph

Mattauch's Double-Focusing Mass Spectrograph

A number of other very accurate mass spectrographs have been designed and an example will be described. In Aston's method the beam of charged particles is first made homogeneous geometrically by means of a collimator and is then deflected and focused electromagnetically. Hertzog and Mattauch investigated theoretically [1] all arrangements of a radial electric field and a homogeneous magnetic field for which both direction and velocity focusing can be obtained, and found it was possible to arrange the system so as to make collimation unnecessary and give the optical analogue of focusing a single slit. Mattauch's apparatus [2] is shown diagrammatically in Fig. 6 (IV^{3}).

It gives theoretically perfect double focusing along the whole length of the plate. The sequence of the fields is the same as in Aston's first mass spectrograph, but the position of the magnetic field in respect to the plate is quite different. A pencil of rays emerging from the fine slit S is deflected by a radial electric field through an angle $\frac{\pi}{8}\sqrt{2}$. It then passes through the controlling diaphragm B and is deflected in the opposite direction through 90 degrees between the pole-pieces of a large electromagnet, shaped as shown, to focus on a photographic plate which lies on the edge of the magnet. The plate is 298 mm. long and a sharp focus is obtained along the whole length. The displacement follows a square root law exactly, and masses ranging from 1 to 10 can be recorded simultaneously over three octaves of mass, an enormous range compared with that of other instruments. The dispersion coefficient is comparatively small from 0·35 to 1·8 mm. for 1 per cent difference of mass, but for doublet measurement of high precision this is offset by the almost incredible sharpness of the lines obtained on Q

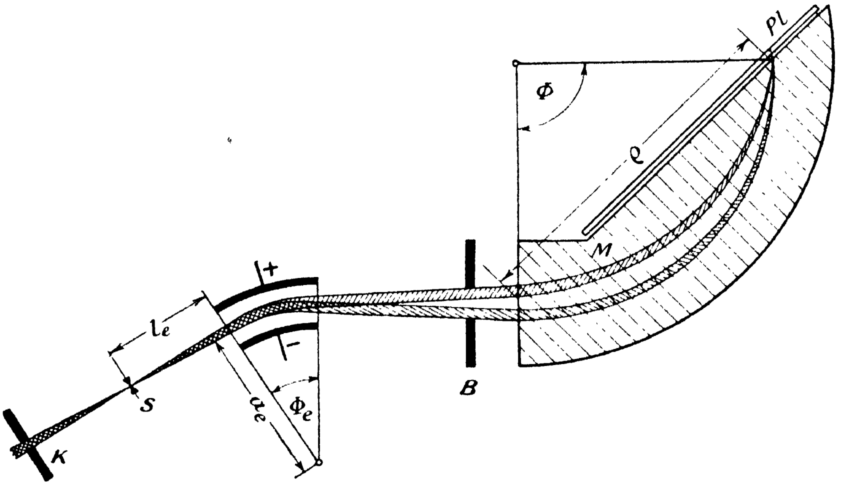

FIG. 6 (IV^{3})
Mattauch's double-focusing mass spectrograph

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[1] *Zeit. phys.*, 1934, *89*, 447, 786.

[2] *Phys. Rev.*, 1936. *50*, 617.

plates, the relative position of which is estimated to 0·0003 mm. By measuring the same doublet at many different points, over a very wide degree of dispersion, Mattauch has turned his double-focusing instrument to a great variety of important researches. One of them is the investigation of numerous bands. By photometry he has established the isotopic abundance of many elements including molybdenum, europium, and lutecium, in which he discovered the new isotope 176, and a variety of common and radiogenic leads. His latest figures for the isotopic weights of the most important substandards are :

^{1}H . . .	1·008130 ± 0·0000033
^{2}D . . .	2·014722 ± 0·0000024
^{12}C . . .	12·003861 ± 0·000024

The large excess mass of H and D is most convenient technically, for it results in the doublets provided by ordinary and ‘ Heavy ’ hydrocarbon molecules with the atoms of the elements being wide enough for easy resolution. Jordan has described [1] results obtained with an instrument using velocity selection in addition to double focusing. He gets a dispersion coefficient of 14·6 mm. (*cf.* M’s 1·4) for 1 per cent difference of mass : the resolving power is increased nearly five times (to 30,000) and the accuracy ten times to one in 10^6.

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[1] *Phys. Rev.*, 1940, *58*, 1009.

SECTION 2: APPLICATION

Petroleum is becoming increasingly important as a source of organic compounds some of which have previously been derived from other raw materials, and others which have hitherto not been available commercially.

It has therefore become of increasing importance to have at hand a ready and reliable means of making an accurate and rapid analysis of the complex mixtures of hydrocarbons which are encountered in practice. The method previously available consisted in fractionation with a very efficient still head: this method, while it gives good results, is time-consuming. The Consolidated Engineering Company[1] have therefore produced the 'Consolidated Mass Spectrometer' which enables the necessary analyses to be made with sufficient accuracy and in a much shorter time. It is well known that with a substance such as, for example, methane, the mass spectrum as well as showing the mass 16 for CH_4^+, will show the masses of such breakdown products as CH_3^+, C^+, &c, and also the low values for those particles which have a double charge and this alone might be expected to lead to difficulties when complex mixtures are in question. But, at first sight, even greater difficulties might be anticipated when we are dealing with mixtures containing isomers such as normal and isobutane. Here the masses of the substances themselves and those of their breakdown products would be identical for corresponding pairs. Investigation has shown, however, that all these difficulties can be overcome. This is because it was found by experiment that in the case of a pure compound such as normal butane, when the 'cracking' process takes place in the mass spectrograph which yields a certain amount of breakdown products, the percentage of each product is almost constant so that the mass spectrograph is like that shown in Fig. 7 (IV[3]). Here the amount of each constituent in the 'cracked' mixture is shown vertically and its mass horizontally. The points 58, 44, and 30 corresponding to $C_4H_{10}^+$, $C_3H_8^+$, and $C_2H_6^+$ are marked; other peaks in the curve corresponding to such particles as $C_4H_9^+$, $C_4H_8^+$, $C_2H_5^+$, and at this last point the peak would include $C_4H_{10}^{++}$ if this is present. The point is that the heights of the various peaks are always in the same proportion for *n*-butane. For isobutane quite a different picture is obtained but again it is a fixed picture which is characteristic of isobutane. It is the dependence of the mass spectrum, as we may call it, upon the structure of the molecule that makes it possible to determine the proportions of isomers of a substance. If we had first determined the mass spectra of normal and isobutane, then prepared a mixture of equal amounts of each of the two substances and determined the mass spectrum of this mixture we should find that the height of each ordinate was equal to half that in the normal butane spectrum plus half that in the isobutane spectrum and similarly, *mutatis mutandis,* for any other mixture. It should be possible, then, in this case to work back from the spectrum of the mixture to its composition and this is the case. It will be noticed in Fig. 7 (IV^3) that there are four traces : these are all recorded by the apparatus and differ from one another only in the magnitude of the vertical scale. The top trace has the most open scale and if we call the sensitivity of this unity the sensitivities of the lower scales are successively one-third, one-tenth, and one-thirtieth. Since the heights of the ordinates are measures of the abundance of the constituents, the device of the four scales enables the height of any one peak to be estimated with an accuracy of 1 per cent over a range in magnitude from 1 to 150.

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[1] **Pasadena, California.**

Principles of Analysis. It is first necessary to determine the mass spectrum of each constituent of the mixture, starting with the pure constituent. This is only necessary to be done once with the given instrument. The resolution of the mass spectrum of a mixture looks a formidable problem when each peak may be a summation of six or more constituents. Fortunately it is not necessary to resolve every peak in order to determine the composition of the mixture. The peaks not so used can be employed as a check on the accuracy of the analysis. They may indicate errors in calculation, instrumental errors or the presence of some constituent not taken into account in the calculation : with the help of this last, unsuspected constituents of mixtures have been discovered. To illustrate the method of analysis an example is given of a simple case. A great deal of work has been done on the simplification of the methods of computation in the case of more complex mixtures, and the manual explaining these methods is over 100 pages in length.

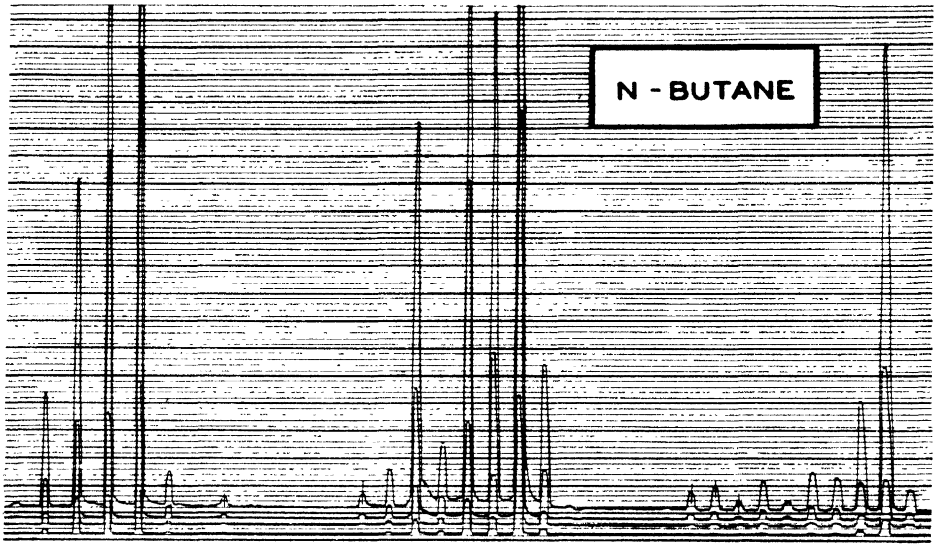

FIG. 7 (IV^3)
Mass spectrograph of *n*-butane

In the example now described [1] the mixture contained only the five constituents methane, ethane, propane, and the two butanes. The mass spectra of these five components had been previously determined and the mass spectrum of the mixture gave the results shown in the first two columns of the following table :

I Mass	II Peak height	III normal butane	IV iso-butane	V propane	VI ethane	VII methane	VIII Σ III- VII	IX II VIII
15	167·3	1·0	1·6	30·4	23·0	110·3	166·3	+ 1·0
16	134·4	0·0	0·0	0·9	0·8	132·7	134·4	0·0
26	146·1	1·6	0·9	37·6	106·4	—	146·5	– 0·4
27	361·6	10·8	12·1	183·0	158·0	—	363·9	– 2·3
28	777·8	9·3	1·2	275·3	494·0	—	780·2	– 2·4
29	593·1	12·5	2·6	467·8	105·6	—	588·5	+ 4·6
30	130·0	0·3	0·0	10·0	119·7	—	130	0·0
31	2·4	—	—	—	2·5	—	2·5	– 0·1
38	24·0	0·5	1·2	21·9	—	—	23·6	+ 0·4
39	98·0	4·3	8·7	84·6	—	—	97·6	+ 0·4
40	14·7	0·6	1·3	13·0	—	—	14·9	– 0·2
41	94·1	9·0	18·9	65·8	—	—	93·7	+ 0·4
42	49·9	3·9	15·6	30·2	—	—	49·7	+ 0·2
43	207·4	32·2	49·8	124·5	—	—	206·5	+ 0·9
44	145·3	1·0	1·6	142·7	—	—	145·3	0·0
45	4·6	0·0	—	4·6	—	—	4·6	0·0
50	0·6	0·3	0·3	—	—	—	0·6	0·0
51	0·5	0·3	0·3	—	—	—	0·6	– 0·1
52	0·1	0·1	0·1	—	—	—	0·2	– 0·1
53	0·6	0·3	0·3	—	—	—	0·6	0·0
54	0·1	0·1	0·0	—	—	—	0·1	0·0
55	0·7	0·3	0·2	—	—	—	0·5	+ 0·2
56	0·5	0·3	0·2	—	—	—	0·5	0·0
57	2·5	0·9	1·6	—	—	—	2·5	0·0
58	5·0	3·8	1·2	—	—	—	5·0	0·0
59	0·2	0·2	0·0	—	—	—	0·2	0·0

Calculation of percentage of *n*- and isobutane (p_n and p_1).

From peak 57 . . . $\underline{0{\cdot}503}\; p_n + 0{\cdot}654\; p_i = 2{\cdot}5$

,, ,, 58 . . . $\underline{2{\cdot}10}\; p_n + 0{\cdot}498\; p_i = 5{\cdot}0$

Solving these two equations gives

Per cent *n*-butane . . . . = 1·8
,, ,, isobutane . . . . = 2·4
,, ,, propane (145·3 – 1·0 – 1·6) $\underline{0{\cdot}269}$ = 38·4
,, ,, ethane (130 – 0·3 – 0·0 – 10·0) $\underline{0{\cdot}3175}$ = 38·0
,, ,, methane (134·4 – 0 – 0 – 0·9 – 0·8) $\underline{0{\cdot}146}$ = 19·4

The underlined coefficients are obtained from calibration and the percentages are gram molecular.

In making these calculations it is known that in the case of peaks 57 and 58 the only constituents which have contributed to these two peaks are the two butanes: the proportion which each butane contributes to each peak is known from the mass spectra of the pure butanes and the underlined numbers are the coefficients obtained from this source.

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[1] Washburn, Wiling and Rock, *Ind. Eng. Chem. Anal.*, 1943, *15*, 541.

Now, knowing the percentage of *n*- and isobutane and having their calibration spectra it is a simple matter to calculate the contribution of each of them to all the peaks and this is done in columns III and IV.

Next, turning to the mass 44, if we subtract from this peak the contributions made by *n*- and isobutane we get the remainder which is due to the propane in the mixture. From the mass spectrum of pure propane, we get the underlined figure 0·269, the sensitivity in per cent division which is used in the calculation of the percentage of propane in the mixture. Knowing this and with the aid of the mass spectrum of propane we can then fill in the figures in column V.

For the mass 30 the contributions of the butanes and propane are subtracted and the result is multiplied by the sensitivity 0·3175 obtained from the pure ethane spectrum.

A similar procedure as shown in the last equation gives the percentage of methane.

Provided that the apparatus is perfect, that no errors occur in the computation and all the constituents of the mixture are taken into account, we should find that in the case of every peak the sum of the heights due to the various components which we have calculated in columns VI and VII should add up exactly to the height of the peak shown in column II: the summation has been made in column VIII and the difference between column VIII and column II is shown in the last column.

In the case of masses 58, 57, 44, 30, and 16 the method of calculation results in the residuals being zero, but with all the other peaks the values of the residuals are a check on the accuracy of the analysis. The small residuals in the example given indicate a satisfactory analysis. In actual use the appearance of comparatively large residuals has enabled the presence of unexpected constituents to be detected.

Principle of the Instrument

The spectrometer is of the Dempster or 180° type. Its operation is schematically illustrated in Fig. 8 (IV^3). Gas is admitted to the ionization chamber through the gas inlet line. The filament, *a*, emits electrons which produce a charge on some molecules and break others into fragments which retain an electric charge. The gas is thus ionized. Electric fields formed by electrodes *d*, *e*, and *f* cause the charge fragments or ions to pass through slits in *e* and *f*. A magnetic field enclosing the region between *f* and *c* forces the ions to move in semi-circular paths. The radius of the path followed by each ion is a function of its mass number, heavy ions following a path of larger radius than light ions. Ions of the same mass number are segregated in a beam of the same radius. The electric fields formed by electrodes *d*, *e*, and *f* are varied so as to contract continuously the radii of the ion beams, thus causing the beams to appear in sequence at the collector *c* after they have traversed a semi-circle (180°). The current collected at *c* from a given beam is proportional to the rate of formation in the ionization chamber of ions of the given mass number. This current is amplified and recorded automatically on photographic paper, thus yielding a complete mass spectrum of the material introduced into the ionization chamber.

Description of the Apparatus

In the design of the Consolidated Mass Spectrometer automatic features have been introduced for ease of operation, for instrument protection, and for maintenance of accuracy.

In front of the operator is a table, the control panels, and the equipment cabinets which house the automatic recording apparatus, the automatic mass-marker, and the power supplies with control circuits which furnish voltages to the mass spectrometer—and electromagnet.

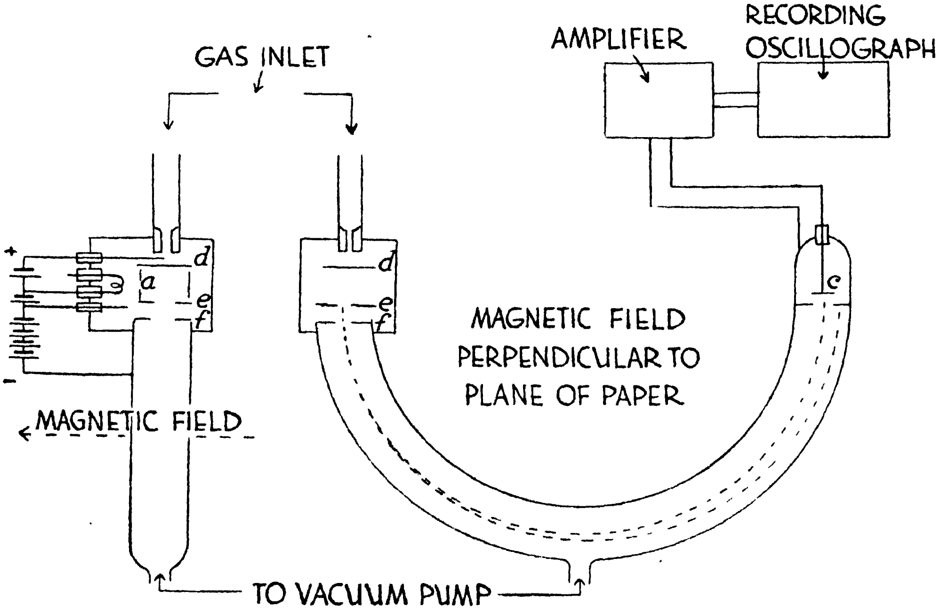

FIG. 8 (IV[3])
Spectrometer of the Dempster type

On the left of the operator is the inlet apparatus for introducing the sample and in between is the electromagnet.

The mass spectra are recorded photographically on sensitized paper in a recording oscillograph. Records are normally 2 to 4 ft. long and an octave of mass units may be recorded in 3½ minutes. As already stated the oscillograph records four traces of different sensitivities. By this method, it is possible to reduce the error in recording to 0·3 per cent of the value recorded for wide variations in the magnitude of peaks.

The mass marker automatically places a mark on the photographic record at predetermined mass values.

The voltage which furnishes the ionization potential is adjustable over a wide range. Standard ionizing current can be maintained above 8 volts.

The positive ion accelerating voltage normally is automatically varied, although it may be adjusted manually so that visual readings may be taken on one indicating meter. The apparatus is operated from a 4·5 KVA 110–220 volt, single-phase lighting circuit.

Scope of the Instrument

Samples containing hydrocarbons up to C_5 can now be determined, isopentane, *n*-pentane, and total pentanes. Traces of C_6 hydrocarbons (0·1 to 1·0 per cent) can be estimated with sufficient accuracy without going through the complete calculations which would be required to separate these constituents. The presence and percentage of oxygen and nitrogen can be obtained. Carbon dioxide interferes and has to be removed and water cannot be determined owing to its adsorption on the walls of the apparatus. Other important mixtures which have been analysed include—

1. C_5 and C_6 paraffins, cyclic, and aromatic derivatives.
2. Determination of benzene, toluene, and xylenes in petrol.
3. Determinations of small amounts of diethyl benzene in ethyl benzene.

Isotope Abundance Measurements. A mass spectrometer of the Nier [1] type has been designed and constructed by Graham, Harkness, and Thode [2] for the identification of isotopes and measurement of their relative abundances. This instrument employs a universal gas-type ion source which may readily be replaced with a furnace or filament-type ion source for use with solids. The instrument is compact and portable with the exception of service connexions and a galvanometer shelf. The electronic units designed for this instrument are described in the original paper. These units operate satisfactorily from unstabilized a.c. and do not require batteries.

The mass spectrometer is capable of detecting isotonic components present to the extent of 1 part in 100,000 of a sample. With the slit dimensions employed, the instrument was found to have a resolving power better than 1 in 130, which agrees with that calculated from the slit dimensions and the radius of curvature.

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[1] *Phys. Rev.*, 1936, *50*, 1041; *Rev. Sci. Instrum.*, 1940, *11*, 212.

[2] *J. Sci. Inst.*, 1947, *24*, 119.

CHAPTER V[3]

MOLECULAR WEIGHTS

SECTION 1: MACRO-METHODS

THE molecular weights of gases may be obtained through Avogadro's law utilizing the relative densities (see chapter on atomic weights). The gram-molecular weight of oxygen (or 'gram-mol') is taken as 32. Avogadro's law is a typical limiting law, and so the lower the pressure at which the gases are measured the more true the law. At low pressures, especially for the permanent gases, the comparison is extremely accurate. Density determination of gases is discussed in Vol. II, pp. 51–62. In addition to the limiting density method, many other methods are available for molecular weight determination of substances.

The lowering of the vapour pressure method
The isothermic distillation method
The raising of the boiling-point method
The lowering of the freezing-point method
The lowering of the transition-point method
The variation of solubility with temperature method
The osmotic pressure method
The ultra-centrifuge method

The Lowering of the Vapour Pressure Method. If p_0 is the vapour pressure of the pure solvent and p is that of the solution, then

$$\log (p_0/p) = \frac{\mathrm{P}.m}{\mathrm{RT}\varrho}$$

where P is the osmotic pressure, m the molecular weight of the solvent in the gaseous state, and ϱ is the density of the solvent. Now

$$\mathrm{P} = \frac{\mathrm{RT}.x}{\mathrm{V.M}}$$

where x is the mass of the solute of molecular weight M dissolved in V litres of the solution; therefore

$$\mathrm{M} = \frac{xm}{\varrho \mathrm{V}} \Big/ \log \frac{p_0}{p}$$

and when the difference between p_0 and p is small this can be written

$$\mathrm{M} = \frac{xm}{\varrho \mathrm{V}} \Big/ \frac{p_0 - p}{p}$$

Raoult's Method. The earliest measurements on the relative lowering of the vapour pressure were made by Raoult, using a barometer tube (Chap. XII, Sect. 8). A small quantity of the solvent was first introduced into the Torricellian vacuum and the vapour pressure of the solvent thus measured; the vapour pressure of the solution was next determined in a similar manner. In this method it is difficult to ensure that the liquids are free from dissolved gases or other volatile substances and to overcome the variation in the superficial concentration of the solution due to evaporation and condensation; furthermore, the concentration of the solution, which is finally in equilibrium with the vapour in the space above the mercury, is not exactly known. The method is no longer used.

Ostwald's Method. An improved method was suggested by Ostwald and carried out by Will and Bredig; it consists in bubbling dry air first through the solution and then through the pure solvent. The air will take up from the solution a quantity of vapour proportional to the vapour pressure thereof and then from the solvent a further amount proportional to the difference of vapour pressure between the solution and the solvent; if the losses of weight w and w_1 of the solution and solvent be determined, we have

$$\frac{w_1}{w} = \frac{p_0 - p}{p}$$

and from this the molecular weight of dissolved substance can be determined.

The solution is placed in three Liebig's potash bulbs, A, B, and C, and the solvent in three more, D, E, and F. Each bulb is weighed and the six are connected together with tubing securely wired on. The six bulbs are wired to a piece of wood and fixed in the thermostat and dry air is aspirated through at the rate of about two or three bubbles per second for 2 hours. The air is dried by passing over soda lime: this can conveniently be contained in two straight tubes 1 in. in diameter and 3 ft. long, placed side by side on a piece of board and connected together at one end by a piece of glass tube. This gives the same result as a very large U-tube, and it can be put at the back of the bench, where it will not occupy much space. After the air current is stopped the bulbs are removed, dried and weighed. Bulbs C and F should show practically no loss, thus indicating that the air was saturated with vapour with respect to their contents: if C shows no loss this means that the vapour pressure of the solution determined is that of a solution having the original composition. The solution in A loses vapour and so alters in composition and has a lower vapour pressure at the end of the experiment than has C, the composition of which has not altered.

Perman's Method. Perman describes a method for determining the molecular weight by the lowering of the vapour pressure in which the apparatus shown in diagram (Fig. 1 (V^3)) is used. In this the inner tube B is exhausted by the water pump; mercury sufficient to act as a gauge is let in and allowed to run into B. The apparatus is again exhausted and weighed. The solution is made up by weight and is introduced by inverting the exhausted apparatus and opening the tap with the end of the tube in the solution. The solute is all washed in with small amounts of the solvent. The tube is then left open and the solution boiled down to half its bulk by heating B. The stopcock is turned, any liquid in the capillary above D removed, and the apparatus weighed to get the weight of the solution. The tube is now heated in the vapour jacket E. After 2 or 3 minutes the tap D is opened and readings are taken from 5 to 10 minutes after B begins to be heated by the vapour. Readings of the heights of the two mercury columns and of the liquid above them are taken. The tip C is then broken and these heights read again to get the relation between the density of the solution and that of the mercury; then

$$m = \frac{w.\mathrm{M}.p.}{\mathrm{W}.d}$$

where m is the molecular weight of the solute
M is the molecular weight of the solvent
w is the weight of the solute
W is the weight of the solvent
p is the barometric height, and
d is the lowering of the vapour pressure

Good results were obtained with ether, chloroform, and water as solvents.

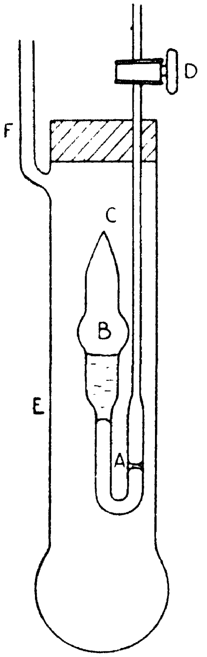

FIG. 1 (V^3)
Perman's apparatus

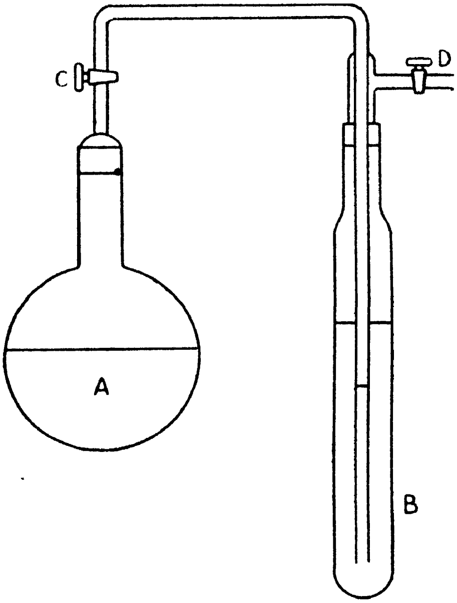

FIG. 2 (V^3)
Wright's apparatus

Wright's Method. Wright [1] uses the apparatus shown in Fig. 2 (V^3). A weighed quantity of solute is placed in B; A and B are half filled with solvent and the apparatus is connected to the filter pump to boil out dissolved gases: after half an hour both taps are closed and the apparatus is allowed to stand for 2 or 3 hours. The tap C is then opened and the difference in height in B is measured. Capillarity is allowed for by opening the ground-joint of the flask A, after which B is removed and weighed to obtain the weight of the solution and so its composition. The molecular weight is then calculated by the ordinary formula, using a value for the vapour pressure of the pure solvent obtained from the tables. In the examples cited in the original paper the average error is about 6 per cent.

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[1] *J. Chem. Soc.*, 1919, *115*, 1165.

Guglielme's and Blackman's Methods. Guglielme[1] describes methods in which the vapour pressures are measured by methods similar to those used in hygrometry; for example, dew-point methods. Blackman uses two graduated test-tubes connected by an inverted T-piece, the arms of which are bent down to form an inverted U, with a bulb in each of the limbs of the ∩. The unknown molecular weight is obtained by comparison with a substance of known molecular weight. The method consists in weighing out 0·05 to 0·1 gram of the substance into one tube and a similar amount of a substance of known molecular weight into the other. The tubes are then half filled with pure solvent, the T-piece connected and the tubes placed in a bath and heated to about 2° or 3° above the boiling-points of the solutions. Readings of the volumes are taken from time to time, and when the solutions have become isotonic the relation

$$\frac{m_1}{m_2} = \frac{V_2}{V_1}$$

will hold, where m is the molecular weight and V the volume. The best results are obtained by heating the bath to the temperature at which the more volatile solution boils; this solution will slowly diminish in volume while the other solution remains unchanged until equilibrium has been attained, when both will boil together. An accuracy of 3 per cent is attainable.

The Isothermic Distillation Method. The isothermic distillation of a volatile solvent from a solution of low molarity to one of greater molarity gives the basis of a method of determining molecular weights. It was originally developed as a micro-method by Barger,[2] and later developed by Rast and others. These micro-methods are discussed in the next section. A macro-method for vapour pressure measurements on somewhat similar lines has been developed by Robinson and Sinclair[3] which yields comparative results of a very high order of accuracy, and so indirectly gives a method of determining molecular weights. The molecular-weight determination depends on the comparison of the vapour pressure of a solution of unknown molecular weight with that of substances of known molecular weight. The experiment can be carried out under isothermic or isopiestic conditions. Robinson and Sinclair's method involves the gravimetric determination of the change in weight of solvent of two heteromolar solutions contained in separate containers but placed in the same evacuated desiccator. The apparatus, e.g. for the determination of the vapour pressure of potassium chloride or other salt solutions, consists of four silver dishes, gold plated internally, 3·8 cm. square and 2 cm. deep, each dish weighing about 35 grams. Into two of these dishes 2 ml. of potassium chloride solution is introduced while the other two contain a solution of another salt of approximately the same composition. The dishes are placed on a copper block, 2·5 cm. thick, in a desiccator which is evacuated at the beginning of an experiment and then rocked in a thermostat at 25°. Distillation occurs until the two solutions have the same vapour pressure, equilibrium being attained in 24 hours except with the solutions 0·5 M and less in concentration, when periods up to 3 days may be required. The dishes are fitted with flap-lids, held open during an experiment by a wire bridge attached to the exit tube of the desiccator, so arranged that at the conclusion of an experiment the lids can be allowed to fall by rotating the exit tube through a small angle without opening the desiccator. This prevents contamination of the solutions by grease, dust or particles of mist on admitting air to the desiccator. From the changes in weight of the solution it is easy to find the concentrations of the isopiestic solutions, the error being not greater than 0·3 per cent, which corresponds to 0·0005 mm. pressure in a 0·2 M solution. Several experiments in succession can be made with the same solutions.

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[1] *Atti R. Acad. Lincei,* 1901 (5), *10,* 232.

[2] See next section.

[3] *J. Phys. Chem.,* 1933, *37,* 395; *J. Amer. Chem Soc.,* 1934, *56,* 1830.

To illustrate the accuracy attainable, two runs were made with potassium chloride solutions in each dish.[1] The initial and final concentrations are given in the following table:

EXPERIMENT A

Dish	Initial concn., M	Concn. after 23 hours:—
1	4·085	2·179
2	3·102	2·179
3	1·733	2·178
4	0·823	2·178

EXPERIMENT B

Dish	Initial concn., M	Concn. after:—	
		1 day	2 days
1.	0·25	0·2128	0·2155
2.	0·25	0·2122	0·2158
3.	0·22	0·2094	0·2155
4.	0·22	0·2100	0·2156

from which it can be seen that although in the first experiment the initial concentrations differed widely, the final concentrations did not differ by more than one part in 2,000, while in the second experiment the over-all variation was less than one part in 700. The practice was to commence with solutions having vapour pressures as nearly equal to one another as possible, so that the case illustrated by the first experiment is an extreme one designed to test the capability of the method.

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[1] *Loc. cit.*

The materials employed were the purest obtainable and were in most cases purified further by recrystallization.

A semi-micro isothermal distillation method has been developed by Signer,[1] for molecular weight determinations. It requires less material than with the above procedure. The technique has been simplified by Clark.[2] The process consists in permitting two solutions in an evacuated system with solvent vapour in contact, to arrive at vapour pressure equilibrium by isothermal distillation. The apparatus is shown in Fig. 3 (V^3). Measurements were made with 1·5 to 1·7 ml. of liquid. The solution is usually 0·1 molar. The samples of the standard reference substance and of the unknown material are made up in the form of pellets. These are weighed and dropped through the open side-arms of the apparatus, so that one bulb receives the standard and the other the unknown. The filling-tubes are then constricted near their bases to facilitate subsequent sealing.

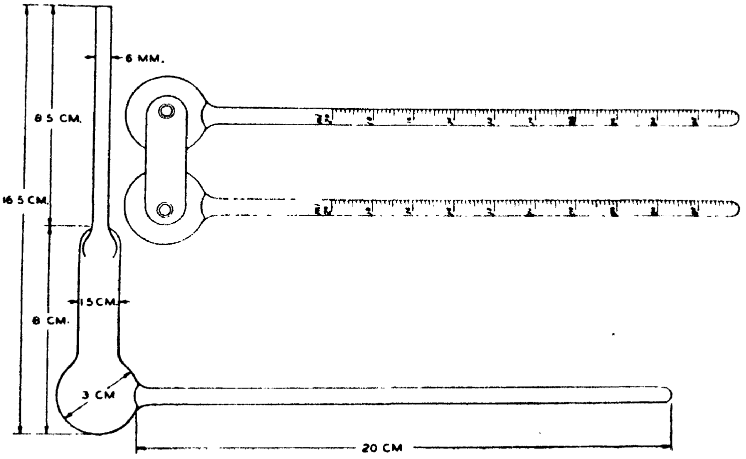

FIG. 3 (V^3)
Signer's apparatus

As soon as the glass cools, 2 ml. of solvent are added to each bulb, after which one tube is sealed at its constriction. As this seal is made, a very gentle stream of dry air should be blown through the tube to prevent vapours of the solvent from coming in contact with the hot glass. The system is then evacuated from a line in which is interposed 1 meter of 1-mm. capillary tubing, and in this manner approximately 0·3 ml. of solvent is distilled from each bulb. While the distillation continues, the constricted part of the connecting-tube is sealed with a soft gas-oxygen flame. The closed evacuated system then contains two solutions containing definite quantities of standard and unknown material arranged as outlined above. Therefore, if the entire apparatus is isothermally insulated, solvent will distil from the solution of greater vapour pressure to the one of less, until equilibrium is established. When this occurs, the volumes of the two solutions will be constant and equimolar. These volumes may then be read by tilting the apparatus and draining the solutions into the graduated side-arms. Five minutes are arbitrarily taken for this purpose.

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[1] *Ann.*, 1930, 478, 246.

[2] *Ind. Eng. Chem. Anal.*, 1941, *13*, 820.

With the data thus available, it follows from Raoult's law that[1]

$$M_1 = \frac{G_1MV}{GV_1}$$

where M, V, and G are, respectively, the molecular weight, volume of solution, and weight of the standard, and M_1, V_1, and G_1 are the corresponding values of the unknown. The volumes are read every 1 to 3 days, depending upon the solvent used, until they become constant.

Boiling-point Method. This method is mainly due to the work of Beckmann. If the vapour pressure of a solvent is lowered by the solution therein of a non-volatile solute, it follows that the boiling-point at atmospheric pressure must be raised a proportional amount. If w grams of a solute of molecular weight M be dissolved in W grams of solvent and the boiling-point is thereby raised ΔT, then

$$m = \frac{K100.w}{W.\Delta T}$$

where K is a constant, the molecular elevation of the boiling-point. K represents the rise in the boiling-point produced by dissolving 1 gram molecule of the solute in 100 grams of the solvent.

Value of K. The value of K can be found by experiment with substances of known molecular weight, and can be calculated from the relation

$$K = \frac{0{\cdot}02T^2}{l}$$

where T is the absolute boiling-point of the solvent and l is the latent heat of vaporization per gram of the solvent.

Values of K for some of the more frequently used solvents are:

Solvent	Boiling-point	Ebulliscopic Const.*	Reference
Water	100°	5·2	Beckmann, *Zs. ph. Ch.*, 1891, *8*, 223
Ammonia . . .	– 33·46°	3·4	Franklin and Kraus, *Amer. Chem. Jour.*, 1899, *21*, 13
Carbon disulphide .	46·3°	23·7°	Menzies and Wright, *J. Amer. Chem. Soc.*, 1921, *43*, 2320
Chloroform . . .	61·2°	36·6	Beckmann, *Zs. ph. Ch.*, 1890, *6*, 437
Acetone	56·3°	16·7	,,
Ether.	35°	21·1	,,
Ethyl alcohol . .	78°	11·5	,,
Benzene	80·3°	26·7	,,
Ethyl chloride . .	12·5°	19·5	Beckmann, *Zs. anorg. Ch.*, 1907, *55*, 371
Ethyl bromide . .	37·7°	25·3	Beckmann, Fuchs and Gernhardt, *Zs. ph. Ch.*, 1895, *18*, 107
Ethyl iodide . . .	41·3°	41·9	,,
Propyl alcohol . .	94·8°	15·8	,,
Isobutyl alcohol. .	104·6°	19·4	,,

* For 1 mol. of solute in 100 grams of solvent.

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[1] *Loc. cit.*

Solvent	Boiling-Point	Ebulli-scopic Const.*	Reference
Isoamyl alcohol . .	131·5°	25·75	Beckmann, Fuchs and Gernhardt, *Zs. ph. Ch.*, 1895, *18*, 107
Methyl formate . .	32·3°	15·05	„
Ethyl formate . .	53·8°	21·8	„
Methyl acetate . .	56·5°	20·6	„
Ethyl acetate . .	75·5°	27·9	„
Methyl propylketone	102°	31·4	„
Ethylene chloride .	82·3°	31·2	„
Ethylidene chloride .	57°	32	„
Menthol	212°	61·5	„
Menthone . . .	206°	21·8	„
Camphor	204°	60·9	„
Naphthalene . . .	218°	58	*Z. physik. Chem.*, 1914, *89*, 111
Acetic acid . . .	118°	29·9	Beckmann, *Zs. ph. Ch.*, 1906, *57*, 129
Propionic acid . .	139·6°	35·1	„
Butyric acid . . .	163·2°	39·4	„
Methyl alcohol . .	67°	8·8	Paal, *Ber. Chem. Ges.*, 1892, *25*, 1234
Formic acid . . .	101°	34·2	Cuisa, *Gazz. Chim.*, 1911, *41a*, 688
Amyl acetate . .	142°	48·3	Beckmann, *Zs. ph. Ch.*, 1907, *58*, 543
Methylal	41°	20·4	„
Methyl sulphide . .	37·5°	18·5	Werner, *Zs. anorg. Chem.*, 1897, *15*, 1
Ethyl sulphide . .	91°	32·5	„
Aniline	184°	32·2	Beckmann, *Zs. ph. Ch.*, 1891, *8*, 223
Cyclohexane . . .	81·5°	27·5	Muscarelli and Musalty, *Gazz. Chim.*, 1911, *41a*, 80
Quinoline . . .	232°	56·1	Beckmann, *Zs. anorg. Chem.*, 1906, *51*, 237
Nitro-benzene . .	205°	50·4	Biltz, *Mon. Chem.*, 1901, *22*, 627
Piperidine . . .	105°	28·4	Werner, *Zs. anorg. Chem.*, 1897, *15*, 1
Benzonitrile . . .	191°	36·5	„
Acetonitrile . . .	80·5°	17·3	Bruni and Salu, *Gazz. Chim.*, 1904, *34b*, 481
Phenol	183°	30·1	R. Meyer and Jager, *Ber. Chem. Ges.*, 1903, *36*, 1555
Thymol	230°	68·2	„
Fenchone . . .	192·5°	59·4	Runini and Olivari, *Gazz. Chim.*, 1907, *37b*, 229
Pyridine	111·5°	27·1	Walden and Centnersagwer, *Zs. ph. Ch.*, 1906, *55*, 324
Carbon tetrachloride	78·5°	48	Beckmann and Stoch, *Zs. ph. Ch.*, 1895, *18*, 107

* For 1 mol. of solute in 100 grams of solvent.

Beckmann Apparatus. One form of Beckmann's apparatus is shown in Fig. 4 (V^3). It consists of a three-necked flask with a piece of thick platinum wire sealed through the bottom. The bulb is half-filled with glass beads, which, with the platinum wire, promote steady boiling and tend to prevent local overheating. The centre neck carries a condenser fitted with a guard tube containing calcium chloride, and the lower end of the condenser passes down into the solvent at a point remote from the bulb of the thermometer. A small hole in this tube near the top of the flask allows the vapour to pass into the condenser. The thermometer passes through the shorter of the two side-tubes, while the longer serves for the introduction of the solute. The flask containing the beads but without the condenser and thermometer is corked and weighed to 0·01 gram; solvent is introduced to fill the bulb nearly two-thirds full and the weighing is repeated. An asbestos jacket is then placed on the flask, the thermometer and condenser fitted, and the flask gently heated with a small flame so that the solvent drips from the condenser at the rate of about 6 drops per minute. The boiling is continued for about 40 minutes to remove all dissolved gases, and then the reading of the thermometer is taken at intervals of 5 minutes, tapping the thermometer before each reading to prevent the mercury sticking. When the temperature has become constant, which may take a long time, the solute is added through the side-tube and readings are again taken until they become constant. Further quantities of the solute may be added and the readings repeated. Solids are usually made into small tablets by means of a steel press before weighing. Liquids are weighed in a pipette supplied with the apparatus, and after the liquid has been introduced the weight added is found by reweighing the pipette.

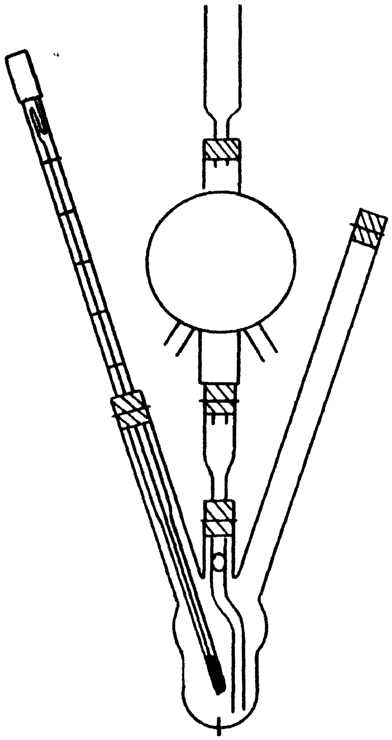

FIG. 4 (V^3)
The Beckmann apparatus

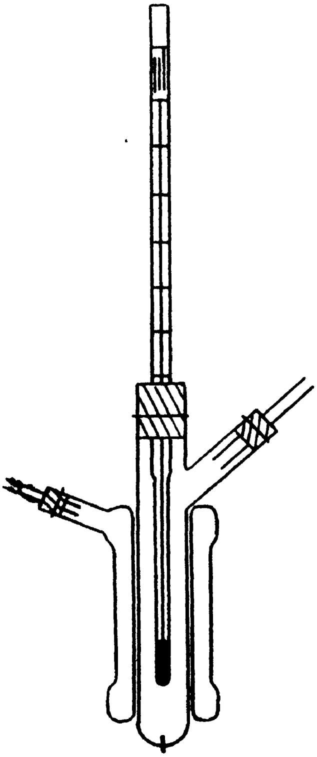

FIG. 5 (V^3)
Improved form of the Beckmann apparatus

Improved Form of Beckmann Apparatus. An improved form of Beckmann apparatus is shown in Fig. 5 (V^3). Here the test tube containing the solution is surrounded by a glass or porcelain jacket containing boiling solvent and fitted with a condenser, so that the tube is surrounded by a jacket of vapour. The inner tube is prevented from touching the jacket by a layer of asbestos paper at the bottom. The jacket contains some pieces of porous tile to promote regular ebullition. The inner tube has a stout piece of platinum wire sealed through the bottom. This tube is fitted with corks and weighed ; 20 ml. of solvent are added and the tube weighed again. The thermometer is fixed in position and glass beads, garnets or platinum tetrahedra are added so as completely to cover the bulb of the thermometer and to come about half-way up the liquid. The condenser having been inserted, a piece of asbestos paper is wrapped round the lower end of the test tube and this is fitted into the jacket, which contains 20 ml. of the solvent, and the jacket is placed on the stand. The stand is made of asbestos board and is heated by two Bunsen burners placed in the two corners opposite the asbestos chimneys. The heat passes chiefly to the jacket, the central tube being mainly heated by radiation therefrom except in the case of liquids of high boiling-point, when a small flame is placed directly under the central tube. Measurements are carried out in the manner already described. A small correction of from 0·2 to 0·35 gram, according to the boiling-point of the solvent, may be applied to the weight of the solvent to allow for that which is in the condenser, &c. The steadiness

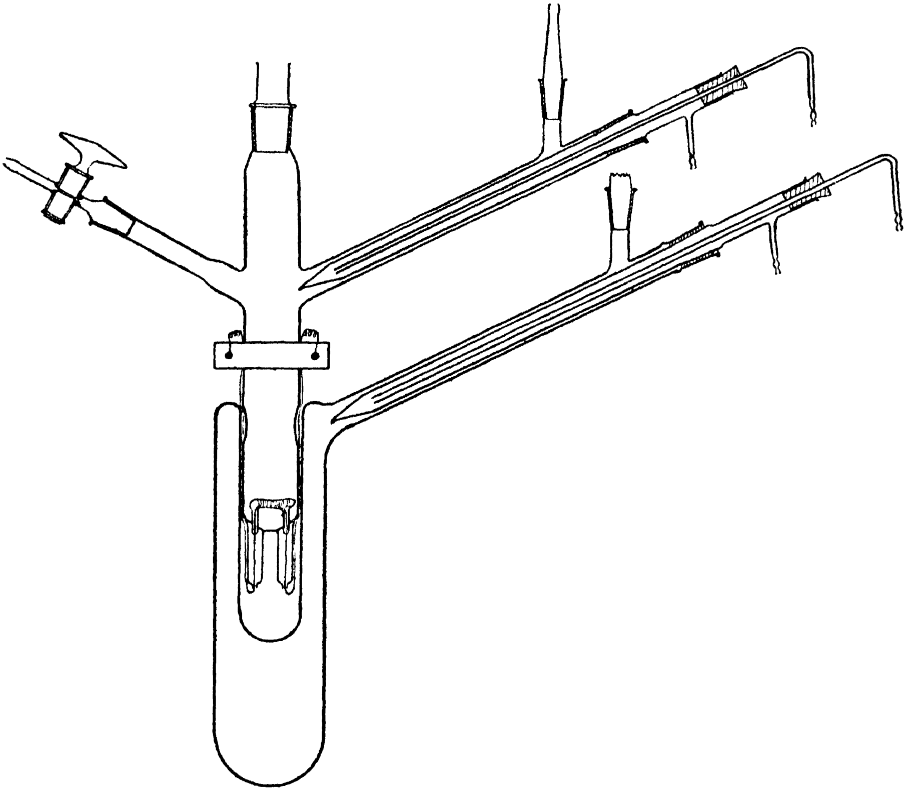

FIG. 6 (V[3])
The Beckmann apparatus with electric heating

of the thermometer reading is much improved by surrounding the thermometer bulb with a cylindrical shield of platinum.

Another form of accurate boiling-point apparatus is shown in Fig. 6 (V^3). This form was made by Hanff and Buest (Berlin) and has been used by Reilly and Buckley. It consists of an inner cylindrical boiling-tube, containing a heating coil of wire, which holds the solvent and the lower half of the tube projects into a hollow vessel also cylindrical and containing the same liquid. The boiling-tube has two limbs, the longer one has an inner condenser and erect valve; the shorter limb is wider near the main tube joint and is used to introduce the solute. It is lagged with cotton wool upwards from its waist, where it fits the outer tube, and along each limb. A Beckmann thermometer introduced through the top stopper reaches almost to the heating-coil. The outer vessel is hollow so as to fit over the boiling-tube and the solvent it contains is refluxed in a side limb similar to the longer limb of the boiling-tube. An airtight chamber is made when the boiling-tube is pushed into the outer tube. The heating is by an oil-bath which boils the solvent in the outer jacket, and the air in the air-chamber is thus maintained at the temperature of the boiling solvent. Electrical heating is essential to raise the solvent in the boiling-tube to boiling and further to increment the temperature when the solute is introduced. In a particular experiment using water as a solvent, 25 ml. were introduced into the boiling-tube and the oil-bath was maintained at 110°. This pre-heating continued for more than an hour when the solvent in the boiling-tube reached about 90°. A current of 1·5 amp. then sufficed to heat the solvent to the boiling-point. The current was switched off momentarily while the solvent was being introduced. A concentration of solute of 1 per cent in solution was arranged and readings of the Beckmann were taken before and after introducing the solute. A steady barometer during the experiment is necessary.

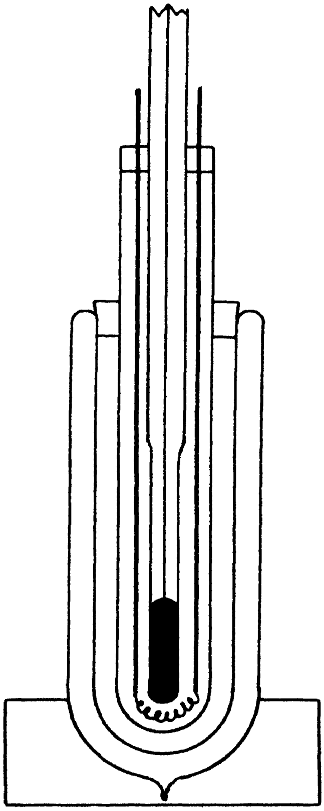

FIG. 7 (V^3)
Another form of the Beckmann apparatus

Other Modifications. A form of the apparatus adapted for electrical heating is shown in Fig. 7 (V^3). The place of the outer jacket is taken by a Dewar vacuum flask from which the silvering has been removed on opposite sides to form a window. The current is led in by the thick copper leads shown and heats the small platinum spiral at the bottom.

An apparatus for electrical heating which also makes use of the principle of Cottrell's 'vapour pump' is described by Palmer.[1]

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[1] *Experimental Physical Chemistry*, Camb. Univ. Press, 1941, pp. 124–6.

The apparatus consists of three parts, a boiling-tube similar to that used in the Beckmann apparatus, with a condenser, but no platinum wire sealed in the bottom, the thermometer and the heating unit. This is made as follows: A *small* hole *h*, about 1 mm. in diameter, is blown in the wall of a piece of broad thin-walled tubing in the position shown in Fig. 8*a* (V^3). Two short lengths of quill tubing 4, Fig. 8*b* (V^3) are firmly bound by copper wires 3 on opposite sides of the broad tube, one of the tubes being near the hole *h*. A coil 2 is formed at the end of a length of nichrome wire (S.W.G. 26) and is inserted into the broad tube so that the long uncoiled end protrudes through *h* (Fig. 8*b* (V^3)). By now brazing the short lower end of the coil to a copper wire of about the same gauge and inserting the latter into the tube 4, the lower end of the coil is secured in place. The projecting long end of the nichrome wire is passed under and once round the tube 4 and then wound in a tight spiral round the outside of the broad tube and the side-tubes (Fig. 8*c* (V^3)). The outside coil is finally secured as before, by brazing [1] on a copper wire, which is inserted into the remaining side-tube 4. (The brazing is done by twisting the copper wire round the nichrome, moistening the join, and covering it with a mixture of brass filings and borax in about equal bulks; and heating in a small blowpipe flame till the brass filings melt and flow freely.) The lower copper wire 3 is now removed, a cork stopper bored to carry the thermometer, and fitted to the boiling-tube, is pierced by the pointed ends of two stout copper wire leads 5, which are carried down to the heating unit and firmly thrust into the side-tubes 4 beside the smaller

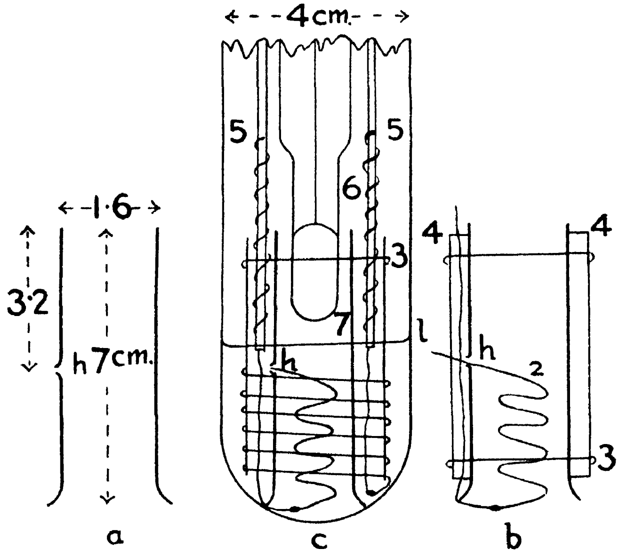

FIG. 8 (V^3)
Arrangement for electrical heating of the Beckmann thermometer

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[1] *Ibid.* The authors desire to thank the Cambridge University Press and Dr. W. G. Palmer for the above description of the electrically heated apparatus.

lead wires from the coils ; the small leads are then twisted round the stouter and their ends soldered to the latter in a position somewhat above their exit from the side-tubes 4. The heating unit is thus securely carried on the stopper, and when this is in position in the boiling-tube the unit should rest on the bottom of the tube, final adjustment being made by sliding the leads 5 in or out of the side-tubes.

The heating current of about 2 amp. may be obtained from the main electric supply by using 32 c.p. carbon lamps in parallel and a small 10-ohm variable resistance. If a Beckmann thermometer is to be used, the stopper should originally be bored for a wide tube, the lower end of which is seen in Fig. 8c (V³) at 6. The thermometer stands in this tube with its bulb in a pool of mercury 7 ; this allows the thermometer to be removed without interrupting the boiling. It is also to be recommended for its steadying influence on the temperature reading.

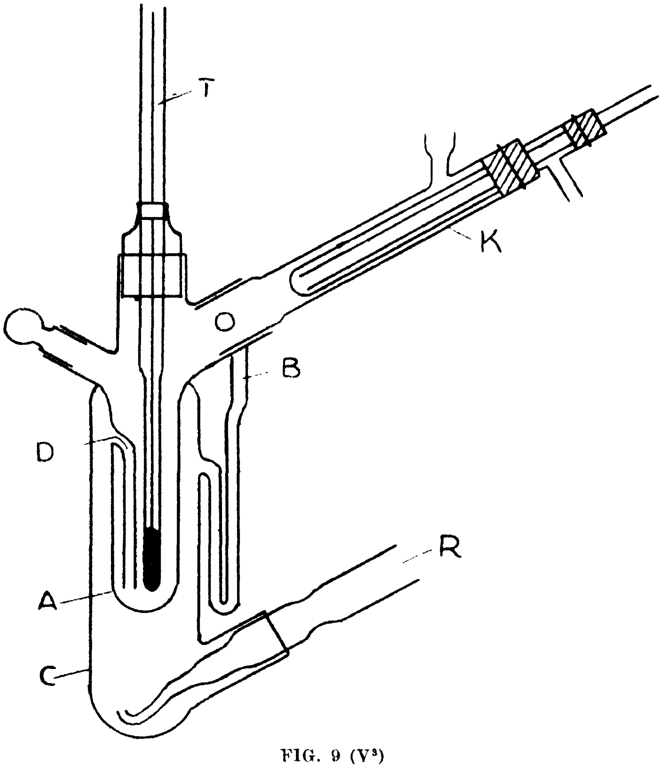

FIG. 9 (V³)
The Beckmann apparatus heated by the vapours of the solvent

The solvent is run into the boiling-tube so that its surface (*l*, Fig. 8c (V³)) is just above the top of the coils and somewhat below the thermometer bulb ; about 35 ml. are required. The liquid is brought to steady boiling by the heating coils, when the thermometer bulb remains for its greater part in the vapour. The temperature is observed at intervals until it has become steady. The heating current is then switched off, and after the vapour has subsided, a weighed amount of solute is added. The heating is resumed and the liquid boiled vigorously until all solid has been washed down from the side-neck, and the solution has become homogeneous. Owing to the fact that nearly all organic solutes lower the surface tension of solvents, the solution will usually foam well up the boiling-tube during this heating. The current is now adjusted by means of the resistance so that the thermometer bulb is enveloped in a continuous stream of foam rising in the broad tube of the heating-unit. The temperature rapidly becomes constant and should remain so even when the rate of boiling is somewhat increased. Electrolysis is quite negligible in an organic solvent, even when the solute is an organic acid, but the method of heating cannot be used for aqueous solutions.[1]

Beckmann has described a further modification of his apparatus (Fig. 9 (V^3)), in which the solution is heated by a current of the vapour of the solvent.

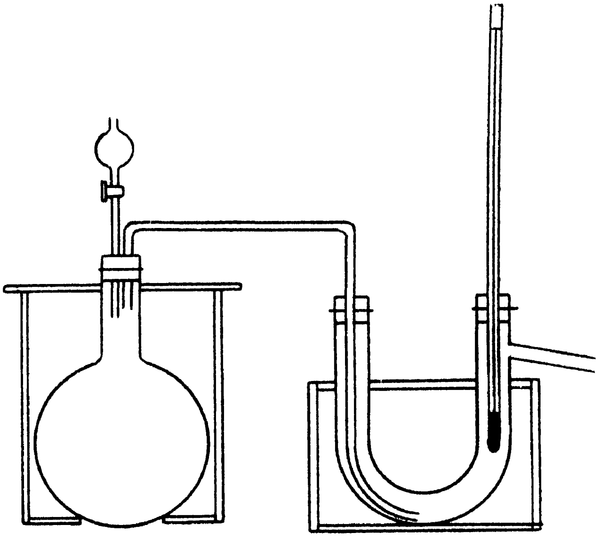

FIG. 10 (V^3)
Sakurai's apparatus

The boiling-tube A is provided with an internal tube D fused in at the side and then passing to the bottom. The boiling-tube is sealed to the other tube C at a point above the opening of the inner tube. The tubulus R is for the addition of solvent to the outer vessel and contains a safety valve. Vapour passes from the outer jacket through the tube D into the solution contained in A. The condensed vapour may be allowed to flow back into A, or by turning K so as to bring the hole therein opposite the end of the tube B, it may be returned to the jacket. The volume of the solution is read off from the graduations on A. Sakurai also describes a method in which the solution is heated by means of the vapour of the solvent. The boiling vessel (Fig. 10 (V^3)) is a U-tube 21 cm. high and 2 cm. internal diameter, with a side-tube for connecting to the condenser. The solvent is boiled in an ordinary round-bottomed flask enclosed in a tinplate jacket to shelter it from draughts, and the vapour is led by a glass tube to the bottom of the U-tube. The latter is enclosed in a box of asbestos board, the bottom being either plain asbestos board with low boiling-point solvents, or having a small hole in it. Glass beads fill the end of the U-tube ; solvent is poured in to a height of 3 or 4 cm. above the beads and the thermometer is inserted. The gas supply to the burners is adjusted so that the volume of solvent in the U-tube remains constant and the readings of the thermometer are taken until a constant boiling-point is obtained. The solute is then added and the boiling-point obtained in the same way.

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[1] Cottrell, *J. Amer. Chem. Soc.*, 1919, *41*, 721; Washburn and Read, *ibid.*, 739.

Differential Method. Barnes, Archibald, and McIntosh use a differential method with two platinum-resistance thermometers of equal resistance, and each made of 1 metre of 0·15 mm. wire wound on a mica frame. The thermometers were sealed into glass tubes and then again into wider tubes containing glass beads and the solvent : the two tubes were heated in an air- or oil-bath and when both were boiling freely the zero-point on the bridge was determined. A weighed quantity of the solute was added to the one tube, and the change of resistance and so the difference of temperature was determined. The composition of the solution was found by analysis. When the elevation of the boiling-point is very small it is often an advantage to use a platinum resistance thermometer instead of the ordinary Beckmann. Thus Linstead and Lowe[1] found that in the ebullioscopic method boiling naphthalene dissolved only 0·4 per cent of magnesium phthalocyanine and the maximum elevation with this substance was 0·04°. The very delicate

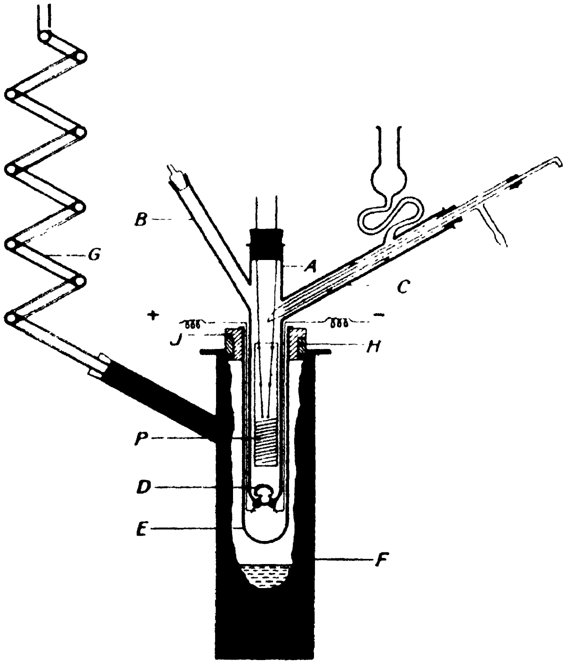

FIG. 11 (V^{3})
The apparatus of Linstead and Lowe

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[1] *J. Chem. Soc.*, **1934**, *145*, 1031.

platinum resistance thermometer employed by them was made from 48 cm. of platinum wire 0·002 in. in diameter wound on thin mica. Fig. 11 (V^3) gives the general set-up of the apparatus. The leads were of silver wire and the measurements carried out by means of a standard Callendar-Griffith's bridge. The thermometer was mounted by means of a moulded asbestos stopper in the inner tube A, of Pyrex glass, which was fitted with two side arms B for the introduction of the solute and C for the condenser and drying tube. Most of the heat required to keep the solvent in A boiling was provided by an outer jacket containing the vapour of boiling naphthalene and the additional heat by a resistance D.

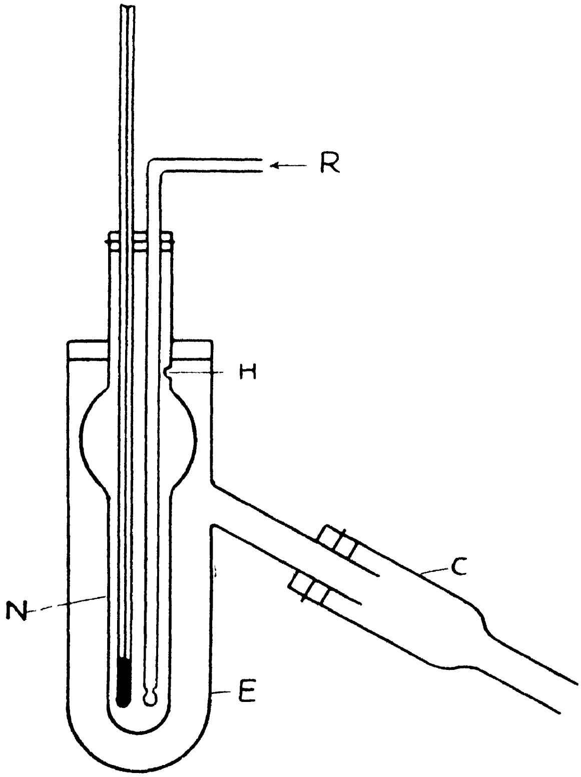


FIG. 12 (V^3)
A modified Landsberger apparatus

Landsberger Method. Walker and Lumsden describe a modification of Landsberger's method, in which the volume of the solution is determined instead of the weight. The apparatus is shown in Fig. 12 (V^3). The outer tube E is connected to a condenser C. The vapour of the solvent passes through R into the inner tube N, which is graduated in millilitres and is provided with a small hole at H to allow the vapour to pass into the outer jacket E. 12 ml. of solvent are placed in N and vapour passed in until it drops from the condenser at the rate of at least one drop in 2 seconds. The thermometer is then read and the heating stopped. The method of heating the solvent in N obviously precludes superheating. The solvent is then poured out until about 6 ml. remain and from 0·5 to 1 gram of the solute is weighed and added. Vapour is then passed in at the same rate as before and the thermometer again read. The flask containing the solvent is at once disconnected, the tube R and the thermometer are removed, the tube N is placed in a glass cylinder which just fits it and holds it vertically, and the volume is read off. The tube is then again fitted to the apparatus, vapour again passed, and a new set of readings taken at the greater dilution. Then

$$M = \frac{K.W}{\Delta T.V.\varrho}$$

ϱ being the specific gravity of the solvent at its boiling-point and W the weight of solute used. A thermometer graduated in tenths of a degree is used, and the determinations are quickly made and are of sufficient accuracy for many purposes.

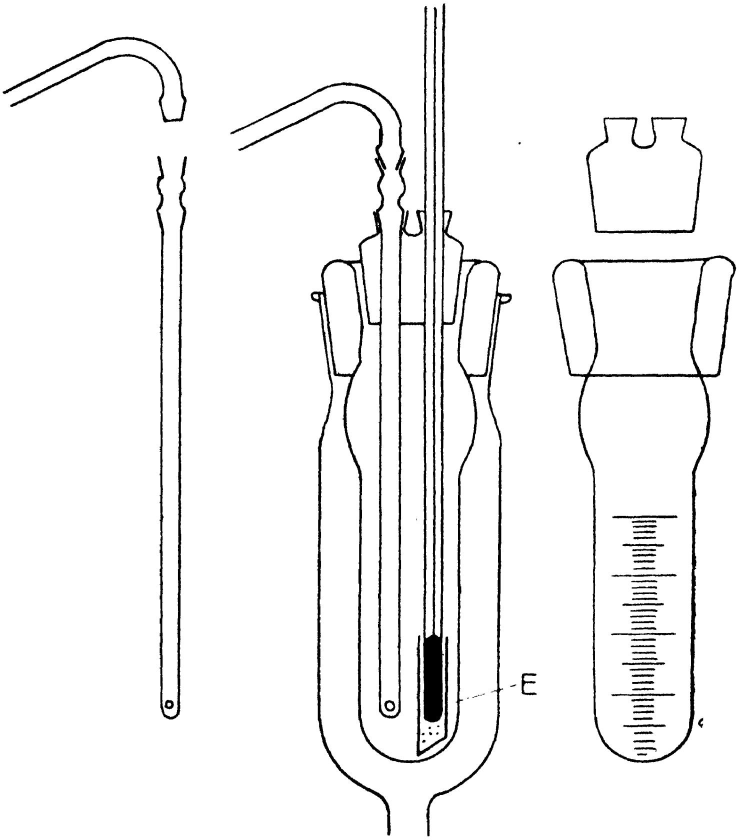


FIG. 13 (V^3)
Another form of the Landsberger apparatus

Erdmann and Unruh dispense with the vapour jacket in Walker and Lumsden's apparatus by using a vacuum flask as jacket.

Turner's modification of the Landsberger apparatus is shown in Fig. 13 (V^3). Glass joints are used so that the apparatus can readily be detached and the measuring tube weighed. The parts of the apparatus are sufficiently indicated in the diagram. The tube E is pierced with a number of small holes and envelops the thermometer bulb to prevent the vapour coming in direct contact with it. The solvent is boiled at a constant rate, e.g. by Sakurai's device of connecting one gas tap to a large and a small burner, both of which are lighted, but the small one alone, which can be regulated independently, being used to heat the flask.

McCoy's Modification. McCoy modified the apparatus shown in Fig. 12 (V^3) by combining the vapour jacket and boiling-tube as shown in Fig. 14 (V^3), where corresponding parts are similarly lettered. The solvent is placed in E and the vapour then passes by the tube R into the solution contained in N and, after passing through this, goes by way of the tube H to the condenser C. The solution in N can be heated in the first instance without increasing its volume by opening the clip K, whereby the vapour leaves without passing through the solution.

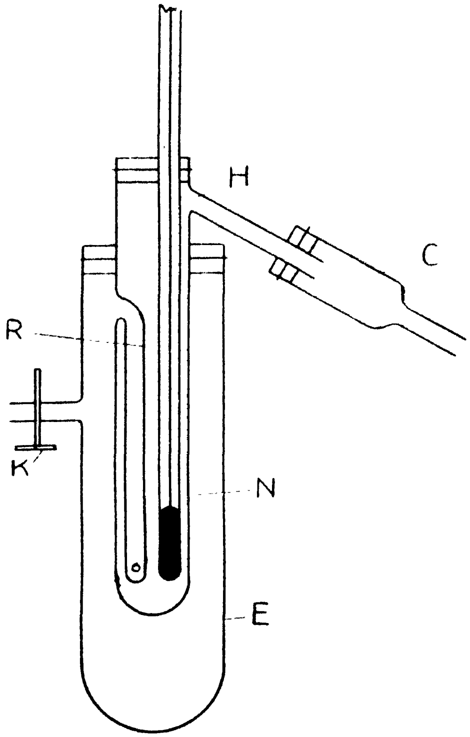


FIG. 14 (V^3)
McCoy's modified apparatus

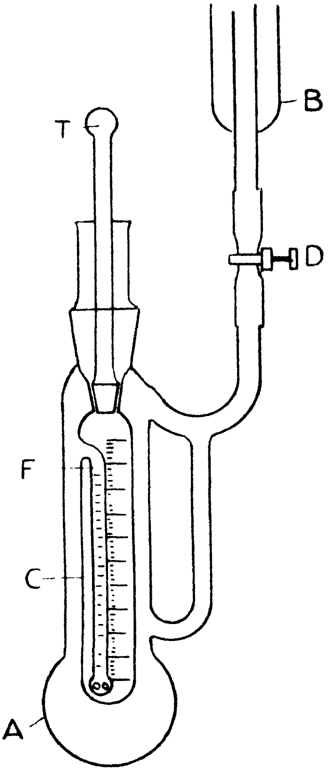


FIG. 15 (V^3)
Menzies' apparatus

Menzies' Method. Menzies describes a method in which the apparatus shown in Fig. 15 (V^3) is used. This consists of a jacket A in which the solvent is boiled, attached to the reflux condenser B and to the inner test tube C. D is a clip on the rubber connexion to the condenser and T is a glass stopper closing the test tube C. The latter has a pressure-gauge tube F graduated in millimetres, while the test tube is graduated in millilitres. In making a molecular-weight determination the bulb of the jacket is filled two-thirds full of the solvent, the empty test tube with the stopper in position is put in, and the liquid is boiled with a small naked flame for 10 minutes under the reflux condenser in order to drive out dissolved gases. The test tube is then removed, filled two-thirds with the boiled-out solvent and put back without its stopper. The liquid in A is boiled for 1 minute to expel air, the clip D is closed so that the vapour bubbles through the solvent in C and so expels air therefrom. The stopper is then placed loosely in the tube, and when it has warmed is pushed home and the clip is opened. A few drops of solvent will have condensed in the tube above the stopper and so have made an airtight joint. The apparatus is now allowed to stand for a few minutes to allow the liquid to fall to the boiling-point under atmospheric pressure, and the difference of level of the liquid in the gauge tube and the test tube is read and taken as the zero reading. If the solvent is pure this reading will be the same as it was before the stopper was inserted: if not, the blowing-through process is repeated. The weighed solid is now introduced into the test tube, preferably in the form of a pastille, and the blowing-through repeated to assist in the solution of the solid and to remove air. The apparatus is allowed to stand for 10 minutes with occasional shaking, the liquid in A being continuously boiled, and the difference in level is again read. After removing any liquid above it by means of filter paper the stopper is removed and the volume of the solution in C read off. Further measurements may be made by adding more solvent to the test tube and repeating the blowing-through.

$$K = \frac{m . 760 . 13{\cdot}6}{1{,}000 . (\varrho - \sigma)}$$

where m is the molecular weight of the solvent as gas
ϱ is the density of the solution
σ is the density of the vapour at 760 mm. pressure and
K is the constant for which values are given below.

$$M = \frac{1{,}000 . W . K . B}{760 . L . V}$$

where M is the molecular weight of the dissolved substance
W is the weight of solute
B is the barometric height
L is the lowering of pressure in mm. and
V is the volume of the solution in ml.

Benzene	K = 1,214
Alcohol	871·5
Water	202·5
Chloroform	620·4
Acetone	1,061
Ether	1,577
Carbon disulphide	526·6

Ludlam's Method. Ludlam describes the apparatus shown in Fig. 16 (V³). The flask A is half-filled with the solvent and is gently boiled.

The vapour passes to the neck of the flask round the tube B and through the small hole G into the space between B and C. Then it descends to the valve *v*, consisting of a small glass bead *w* sealed to a platinum wire, and so into the tube C and away to the condenser. In about 15 minutes the temperature of the solvent which has condensed in C will have become constant, and is read. The thermometer is then raised above the level of the liquid, the bulb A is touched with the hand, which instantaneously stops the vapour bubbling through C, and the volume is read, the valve *v* preventing the liquid from running back into B. A thermometer graduated in tenths of a degree is used.

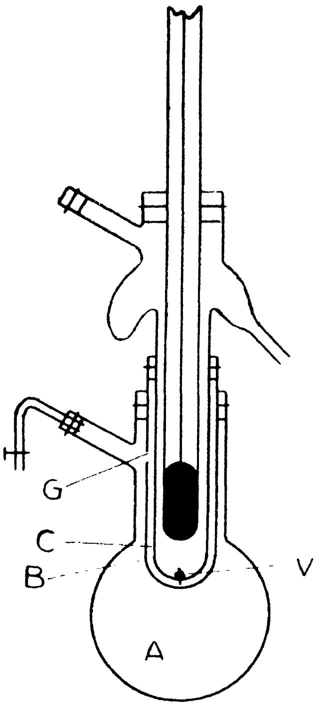
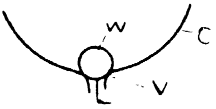


FIG. 16 (V^3)
Ludlam's apparatus



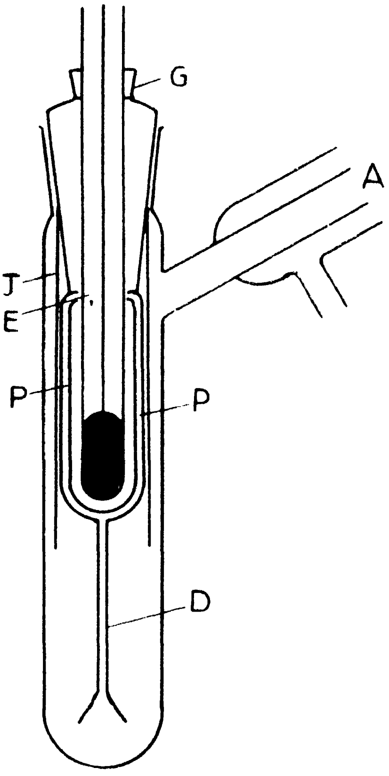


FIG. 17 (V^3)
The Cottrell apparatus

Cottrell's Apparatus. Cottrell[1] pointed out that even if superheating is overcome the temperature indicated by a thermometer bulb immersed in a boiling solution may be as much as 0·1° above the boiling-point at atmospheric pressure on account of hydrostatic pressure. He places the bulb of his thermometer in the gas phase and causes the boiling of the liquid to pump the solution up in such a way as to cover the bulb with a thin film: the constancy and correctness of the thermometer reading is therefore greatly improved, so that it now becomes of greater importance to note and allow for changes in the barometric pressure. Cottrell's apparatus, as modified by Washburn and Read, is shown in Fig. 17 (V^3). The apparatus is constructed entirely of glass, the thermometer being cemented into the ground-glass stopper G. J is a glass sheath carried on the stopper G and protecting the bulb from the cold liquid falling from the condenser A. The pumping apparatus PP is also attached to the stopper. While the solution boils the bubbles of vapour carry solution up to the tube D and squirt it over the thermometer at E. Porous porcelain was used to promote quiet ebullition, and the whole apparatus was protected from draughts by a sheet of asbestos paper. To allow for variation in boiling-points, due to alteration of the barometric height, an apparatus was used on each side; first with solvent alone in both, then with solution in one and solvent in the other. The concentrations were determined by withdrawing portions of the solution by means of a side-tube (not shown). This apparatus is an improvement on that of Beckmann.

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[1] *J. Amer. Chem. Soc.*, 1919, *41*, 721.

The Beckmann Thermometer. In many of the boiling-point and freezing-point methods the temperature changes are very small and are therefore measured with a Beckmann thermometer. On this instrument the degrees are Centigrade degrees divided into tenths and hundredths, so that thousandths of a degree can be estimated. In order that the hundredth of a degree division shall be sufficiently large to allow it to be subdivided into tenths by eye estimation, it is found possible to have a scale of 6° only on a thermomter about 50 cm. long. To cover the ordinary range of boiling-points and freezing-points used in the laboratory, the Centigrade temperatures indicated by a point on the scale are adjustable by means of a small excess of mercury contained in a reservoir A at the top (Fig. 18 (V^3)). Supposing the thermometer is to be set for a boiling-point determination, the boiling-point of the solvent—let this be $t°$—should be indicated by about 1·0 on the scale; if the mercury were to rise to *a* the temperature would be about 6° above the boiling-point $t°$. A bath is therefore maintained at this temperature, $t + 6°$. The thermometer is inverted and given a sharp jerk to force the mercury in A from *b* to *a*; the thermometer is next turned carefully up and the bulb placed in the bath, the mercury then expands and may reach *a* and so connect up to the reserve of mercury. If it does not do so it must be placed in a bath at a higher temperature until the connexion is made. The thermometer is then placed in the bath at $t + 6°$, and after a minute is removed and given a sharp downward jerk which breaks the thread at *a*. On cooling to the temperature $t°$ the mercury should fall to somewhere near the division marked 1·0 on the scale. For a freezing-point determination, where the solvent freezes at $t°$, we want the mercury at about the fifth division when the temperature is $t°$, so that it will be at *a* when the temperature is about $t + 2°$. The bath is therefore maintained at this temperature, and after the mercury column has been joined up to the reserve supply of

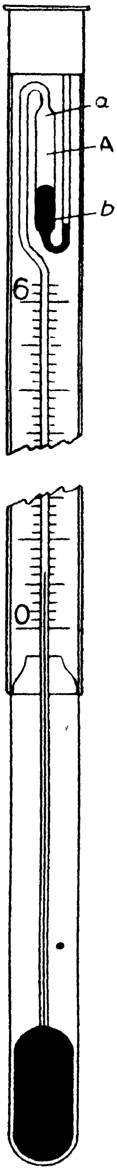

FIG. 18 (V^3)
The Beckmann thermometer

mercury in the reservoir, the procedure which is described above is followed. The thermometer should be set at least 24 hours before it is to be used. Before taking a reading the thermometer should always be tapped with a pencil to prevent the mercury sticking in the narrow capillary tube; an electromagnetic device is sometimes used to tap the thermometer continuously.

Owing to the risk of mercury freezing, at lower temperatures other liquids must be used in the thermometer. The addition of thallium to the mercury to make an 8·5 per cent mercury-thallium mixture gives a liquid that does not solidify until a temperature of − 60° is reached. Liquid pentane thermometers can be used for temperatures as low as − 100°.

Determination of Molecular Weights using Small Quantities of Substance. Pregl has modified the boiling-point method so that it can be carried out using very small amounts of substance and of solvent. A small boiling-vessel similar in shape to the larger one usually employed is provided and this is carefully heated in a current of hot air. A specially designed tablet press is also employed. Owing to the great reduction in the quantity of solvent taken a suitable rise in boiling-point is obtained in spite of the minute amounts of solute added. Working details are given in the next section.

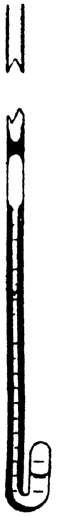

FIG. 19 (V^3) Differential vapour pressure thermometer

Differential Vapour Pressure Thermometer. In the Beckmann method and its modifications there still remains (1) the inherent errors of the Beckmann type of thermometer, (2) the uncertainty as to the concentration of the solution at the moment when the boiling-point is measured due to the fact that some of the solvent is in the vapour state and some present on the walls of the apparatus above the solution, and (3) the difficulty introduced by the alteration of the boiling-point produced by a change of the barometric pressure during the course of the experiment.

These difficulties are overcome by the use of the differential thermometer of Menzies, this (Fig. 19 (V^3)) has two bulbs connected by a narrower tube about 10 cm. long; the lower end of the tube carrying one bulb is bent upwards so that this bulb lies alongside the lower end of the stem. The glass is carried upwards beyond the upper bulb and is expanded at the top so as to give a diameter large enough readily to be fixed in a clamp. The thermometer contains a liquid having an appreciable vapour pressure at the temperatures at which the instrument is to be used; for example, water is a convenient liquid for many purposes.

The stem and the lower bulb are marked in centimetres with subdivisions. If the instrument is clamped in a vertical position and both bulbs are at the same temperature the water will stand at a different height in the lower bulb and the narrow tube, owing to capillarity; this reading is taken as the zero. If one bulb is at a different temperature from the other the difference of vapour pressure causes a change in the heights of the liquid in the instrument; the magnitude of this change serves to determine the difference of temperature of the two bulbs. An alteration of the height of the water column of 1 mm. corresponds to a temperature difference of 0·0313° at

35° and 0·0026° at 100°. Menzies and Wright [1] describe an apparatus for the determination of molecular weights by the rise of boiling-point, using the differential thermometer.[2] This is shown in Fig. 20 (V^3).

The bulb at the bottom is narrowed at the neck and then expands to a second bulb above which is a cylinder narrowed at the top to form the inner tube of the condenser. Inside the wider cylinder is a second glass cylinder open at both ends which acts as a double jacket. The differential thermometer hangs so that its upper bulb is near the top of the wide cylinder and the lower bulb near the bottom of this: the handle is long enough to provide a projecting piece by which it can be clamped. The pump hangs on the lower bulb of the differential thermometer. The boiling-tube is heated directly with a small Bunsen flame, protected by a metal wind shield. Boiling causes bubbles of vapour to pass up the tube of the pump, carrying with them some of the solution, which is thus sprayed over the lower bulb of the thermometer; the upper bulb is in the vapour space, and by condensation of vapour very quickly acquires the temperature of the boiling-point of the solvent. Thus, this bulb is at the boiling-point of the pure solvent while the other bulb is at the boiling-point of the solution, and the difference of these two temperatures is the rise of boiling-point required. Equilibrium is reached very rapidly and the apparatus is not sensitive to the disturbing effects of draughts.

The concentration of the solution is obtained by having the narrow neck above the lower bulb graduated in millilitres: the volume is obtained by stopping the boiling and taking the reading at once while the apparatus is still full of vapour and the walls are wet with the solvent.

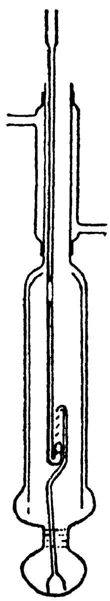
FIG. 20 (V^3)
The apparatus of Menzies and Wright

Determination of the Molecular Weight of Benzil in Chloroform, using the Differential Thermometer. Clamp the apparatus on the stand at a point below the upper side tube of the condenser at such a height that when the top of the Bunsen is 1 cm. below the bulb its base is several centimetres above the base of the stand. Add purified chloroform (*vide ante*) to reach to the lower graduations on the neck. Turn on the condenser water, light the burner, and adjust the flame by means of a screw-clip. Hang an ordinary thermometer inside the apparatus and take the boiling-point of the pure solvent, avoiding an exposed mercury thread; read the barometer so that if there is any change during the experiment the new boiling-point can be calculated. Lower the Bunsen and swing it aside and, as soon as the boiling ceases, read the volume of the solvent. Resume the heating, remove the mercury thermometer, and insert the pump by lowering it from a hook at the end of a long wire. Put the differential thermometer in position and engage the end of the pump with the lower bulb, then clamp the thermometer in position. While equilibrium is being obtained the pastilles of the solute may be prepared. After about 15 minutes take the zero reading, i.e. the difference in millimetres between the readings on the stem and the lower bulb. In making readings parallax errors are avoided by fitting a white card 10 cm. by 7 cm., on which are bold 1 cm. horizontal graduations, at a suitable distance behind the tube, with the graduations at the same level as those on the tube, and placing the eye so that readings on the card and thermometer correspond. The value obtained for the zero reading is a good check on the purity of the solvent. Any unsteadiness in the position of the thread is due to too slow boiling. Weigh the tube containing the pastilles, drop one in at the top of the condenser, and weigh again. As soon as solution is complete the reading becomes constant; read the difference of level and subtract this from the zero reading. Another pastille is then added, and another reading taken for the new concentration.

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[1] *J. Amer. Chem. Soc.*, 1921, *43*, 2314.

[2] The complete apparatus is made by Eimer and Amend, New York, and includes a differential thermometer of pyrex glass containing water.

Since in the present case the volume of the solvent has been determined we require the ebullioscopic constant for 100 ml. of solvent instead of that for 100 grams. This is given in the following table, as is also the temperature difference for 1 mm. change of height in the water column of the differential thermometer at the boiling-points given.

Solvent	Boiling-point	K for 1 gm.-mol. in 100 ml.	Temp. difference for 1 mm.
Acetone	56·3°	22·9	0·01215
Benzene	80·3°	32·0	0·004918
Carbon disulphide . .	46·3°	19·4	0·01858
Carbon tetrachloride . .	76·8°	32·4	0·005558
Chloroform	61·2°	27·7	0·009968
Ethyl acetate	77·2°	33·6	0·005480
Ethyl alcohol	78·8°	15·8	0·005182
Ethyl ether	35·0°	31·1	0·03130
Methyl acetate . . .	57·1°	23·4	0·01175
Methyl alcohol . . .	64·7°	11·8	0·008692

For accurate work the temperature to which the readings of the differential thermometer are to be referred in order to find the conversion factor to be used is that given by the mercury thermometer, plus half the ebullioscopic rise (found approximately in the first instance); the exact factor is then found from Menzies' table (*loc. cit.*).

The Freezing-point Method, also due to Beckmann, has the advantage over the boiling-point method that there is no question of super-heating or pressure effect. The same equations used in the boiling-point method apply, *mutatis mutandis*, to the freezing-point method. The apparatus is shown in Fig. 21 (V^3). A weighed quantity of the solvent is placed in A; the stopper, with the Beckmann thermometer F and a platinum stirrer D, is fitted. The tube A is placed in the wider tube B which serves as an air-jacket, and B is placed in the freezing mixture contained in a large battery jar and stirred with a metal stirrer. The freezing mixture must have a temperature not more than 3° lower than the freezing-point of the solvent. The solvent is weighed out directly into A by fitting this with corks and supporting it in a beaker on the balance pan; 15 to 20 grams, weighed with an accuracy of 0·02 gram, is sufficient. The bulb of the thermometer is placed about half-way down in the solute. An approximate value of the freezing-point is first obtained. The tube A having been placed in B, the solvent is slowly stirred at the rate of about one stroke per second; when solid begins to separate the rate of stirring is increased for a time and then the slower rate is resumed. The mercury will be found to rise when the faster rate of stirring takes place, and the highest point to which it rises is taken as the freezing-point. The tube A is now removed and allowed to warm in the air with vigorous stirring. When all the solid has disappeared the tube is at once replaced in B and slowly stirred until the temperature falls 0·1° below the freezing-point. Freezing is then induced by rapid stirring, and as soon as the temperature begins to rise slow stirring is resumed, the highest point to which the mercury rises being observed, not omitting to tap the thermometer. This procedure is repeated until three readings, agreeing to 0·002°, are obtained. The supercooling should be as small as possible and should not exceed 0·5°. If the solid does not separate with this degree of supercooling a small crystal of the solid is added by the side tube G, and for this purpose a small quantity of the solvent is placed in a test tube immersed in the freezing mixture. The solute, if a solid, is weighed in the form of a pellet, or if a liquid, in the special pipette, and is introduced through the side tube G. The amount used should be sufficient to give a lowering greater than 0·1°. When it has been completely dissolved an approximate value of the freezing-point of the solution is first obtained, and then the more accurate value, in the manner already described for the solvent. Solutions tend to supercool without separation of solid more readily than the solvents, and so it may be necessary to add a crystal of solvent from the small test tube; this is best done by having a rod therein which, when removed, will have a little solid adhering to it. This rod is then inserted through G and the stirrer is raised to touch it, when enough solid will be detached to start crystallization. A second and third determination are made with more concentrated solutions. Solvents such as acetic acid are so hygroscopic that moisture passing in through the aperture through which the stirrer passes is taken up and continuously lowers the freezing-point of the acid. To prevent this Beckmann surrounded the top of the stirrer with a jacket through which dried air was passed, the stirrer being moved by means of a flexible rubber tube.

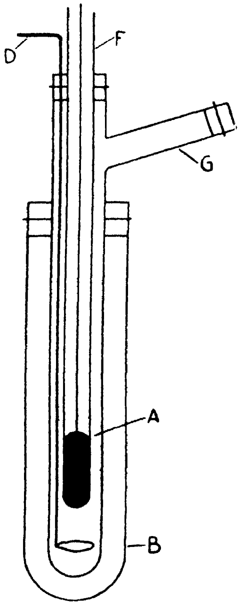

FIG. 21 (V^3)
Freezing-point apparatus

Values of Constant for Lowering of Freezing-point. The values of the constant for some of the more common solvents are given in the table appearing on the next page:

Solvent	Freezing-point	Cryo-scopic Const.	Reference
Water	0°	18·6	Nernst and Abegg, *Zs. ph. Ch.*, 1894, *15*, 681
Formic acid	8°	28	Raoult, *Ann. Chim. Phys.*, 1884, *2*, 66
Acetic acid	17°	39	,,
Nitrobenzene	5·3°	70·5	,,
Formamide	1·8°	38·5	Bruni and Trovanelli, *Rend. Acad. L.*, 1904, *13b*, 176
Acetamide	82°	40·4	Reilly, Wolter and Donovan, *Proc. R.D.S.*, 1930, *19*, 467
Phenol	38°	74	Eykman, *Zs. ph. Ch.*, 1889, *3*, 203
o-cresol	30·5°	56·2	Eykman, *Zs. ph. Ch.*, 1889, *3*, 113
p-cresol	35·9°	77	Eykman, *Zs. ph. Ch.*, 1889, *4*, 497
Thymol	48·2°	80	,,
p-toluidine	39·1°	51	,,
Di-phenyl	70·2°	80	,,
Di-phenyl methane	26·3°	27	,,
Benzophenone	48·1°	98	,,
Urethane	48·7°	51·4	,,
Anethol	20·1°	63	,,
p-bromophenol	63°	112	,,
Stearic acid	61°	45	,,
Palmitic acid	60°	44	Eykman, *Zs. ph. Ch.*, 1889, *3*, 203
Naphthalene	80·1°	69	Auwers, *Zs. ph. Ch.*, 1895, *18*, 595
Benzene	5·5°	51·2	Paterno, *Gazz. Chim.*, 1899, *19*, 640
Aniline	5·96°	58·7	Ampola and Rimatori, *Gazz. Chim.*, 1897, *27a*, 35
Di-benzyl	52°	72	Garelli and Calzolari, *Gazz. Chim.*, 1889, *29b*, 258
Tri-phenyl methane	93°	124·5	,,
Benzylaniline	36·5°	87	,,
o-chlorophenol	7°	77·2	Jona, *Gazz. Chim.*, 1909, *39b*, 289
m-chlorophenol	28·5°	83	,,
p-chlorophenol	37°	85·8	,,
o-bromo-nitrobenzene	36·5°	91	,,
m-bromo-nitrobenzene	54°	87·5	,,
o-nitro benzoic-ester	30°	74	Bruni and Callegari, *Rend. Linc.*, 1904, *13a*, 567
p-xylol	16°	43	Paterno i Montemortini, *Gazz. Chim.*, 1894, *24b*, 197
o-nitro phenol	44·3°	74	Ampola and Rimartori, *Gazz. Chim.*, 1897, *27b*, 31
Di-methylaniline	1·96°	58	Ampola and Rimatori, *Gazz. Chim.*, 1897, *27a*, 51
p-chlorotoluene	7°	56	Auwers, *Zs. ph. Ch.*, 1902, *42*, 513
p-bromotoluene	26·9°	82·1	Paterno, *Gazz. Chim.*, 1896, *20b*, 1
Cyclohexane	6·2°	200	Muscarelli and Benati, *Gazz. Chim.*, 1909, *37b*, 642
Veratrol	22·5°	64	Paterno, *Gazz. Chim.*, 1896, *26b*, 9
Acetophenone	19·5°	56·5	Garelli and Montanari, *Gazz. Chim.*, 1894, *24b*, 229
p-toluic phenyl-ester	32°	62	Auwers, *Zs. ph. Ch.*, 1902, *42*, 513
Phenyl benzoate	69°	80	Gavelli and Gorni, *Gazz. Chim.*, 1904, *34b*, 111
p-iodotoluene	34°	100	Bruni and Padoa, *Gazz. Chim.*, 1904, *34a*, 133
Bromoform	8°	144	Ampola and Manuelli, *Gazz. Chim.*, 1895, *25b*, 91
Resorcinol	110°	65	Gavelli, *Gazz. Chim.*, 1895, *25b*, 173

Some of the solvents are solids at the ordinary temperature, and it will be seen that the constants are very large, so that a thermometer graduated in tenths of a degree may be used instead of the Beckmann. The method of carrying out the experiment is similar to that described, with the exception that the outer vessel C is replaced by a large beaker containing water heated to a constant temperature about 3° below the melting-point of the solvent.

Dioxan has been suggested by Oxford [1] for use as a solvent in the cryoscopic method of determining molecular weights. It is chemically inert and has wide solvent power. Most crystalline organic substances including many natural products other than sugars and amino-acids are soluble in it. Its freezing-point is 11·67° and its molecular depression constant is 47.

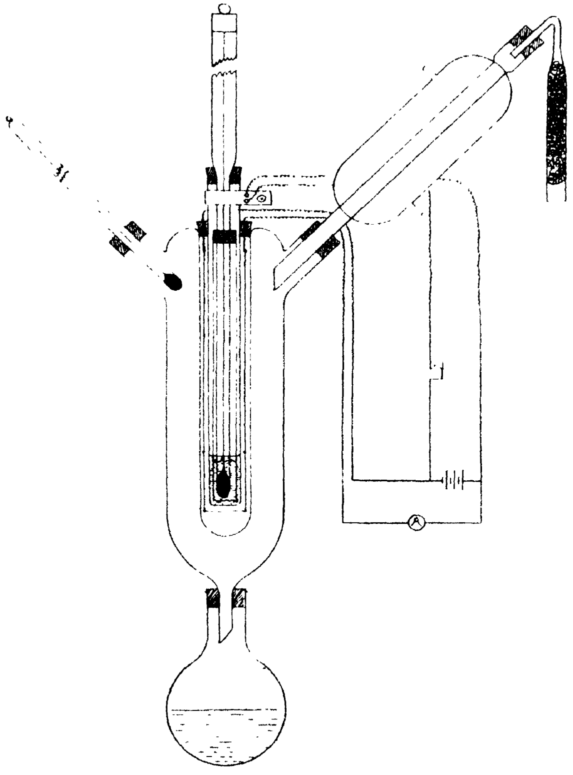

FIG. 22 (V^3)
Modified freezing-point apparatus

Ostwald's Modification. For more exact determinations Ostwald maintains that 500 to 1,000 grams of the solvent should be weighed out into a cylindrical glass vessel surrounded by a higher and wider metal vessel which in turn is placed in a large bath containing the freezing mixture ; the bath is lagged and covered to prevent, as far as possible, heat from passing in. The freezing-point of the solvent is first determined, then a known amount of the solute is added in the form of a concentrated solution after the removal of an equal amount of the solvent. The freezing-point is then again determined. Allowance is made for the amount of solid solvent which separates by a calculation for the degree of supercooling used. If C is the specific heat of the solution, λ the latent heat of solidification per gram, and θ the over-cooling, then the fraction of the liquid which solidifies is r, where $r = C\theta/\lambda$; the concentration of the solution whose freezing-point has been determined is therefore increased from p to $p\ (1 + C\theta/\lambda)$.

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[1] *Biochem. J.*, 1934, *28*, 1325.

In addition to the solvents already mentioned, Morgan and Benson [1] have used melted crystalline hydrates as solvents ; for example, they determined the molecular weight of acetic acid dissolved in melted calcium chloride, $CaCl_2.6H_2O$, for which the freezing-point is 29·48°, and K is 45·0.

The apparatus shown in Fig. 22 (V^3) has been employed [2] also for molecular weight determinations.

Freudenberg [3] working on the molecular weight of triacetycellulose in acetic acid, obtained some remarkable results in experiments at small concentrations, depending upon the procedure employed in the molecular weight determinations of polysaccharides and their depolymerized derivatives. He states that certain low results obtained for molecular weights depended on the degree of supercooling and the delayed speed of crystallization. This is of special importance when small depressions are produced by solution of polysaccharides or non-crystalline substances in the solvent.[4] Freudenberg uses the following method : When melting the crystals of the solvent (e.g. acetic acid) which separate during the molecular weight determination in the cryoscopic method, he raises the temperature only 0·8° to 1° over the melting-point of the acetic acid. In this way a few small crystals of the acetic acid remain unmelted. The temperature is then lowered by the cooling of the outer jacket until the thermometer reads from 0·05° to 0·1° above the melting-point of the acetic acid. Stirring is then commenced by means of the ' make and break ' device. In this way the degree of under-cooling does not go below 0·08° to 0·1° before the mercury thread ascends, and crystallization of the solvent begins. If the under-cooling is greater than the above limits, the mercury will register a higher figure, owing to the fact that a large number of small crystals (with a corresponding larger surface) are formed, and these serve as a quick-heat supplier (' gute Wärme-Nachlieferung '), and, therefore, the mercury rises more quickly. On the other hand, if the degree of super-cooling is less than the above limits the mercury will give a lower reading, as in this case fewer big crystals will be formed, thereby lessening the heat supply, and thus slowing down the rise of the mercury. In consequence, a very long time is required to reach equilibrium. The temperature of the outside bath, of course, also affects the speed of crystallization since the degree of super-cooling is largely dependent on this external temperature.

The period from the time when the mercury starts to ascend until it reaches its maximum point should be the same in the case of the solvent alone and with the polysaccharide in solution. The same procedure is adopted with the solute in solution as that in the case of the blank or control.

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[1] *J. Amer. Chem. Soc.*, 1907, *29*, 1168.

[2] Reilly, Wolter, and Donovan, *Sci. Proc. Roy. Dub. Soc.*, 1930, *19*, 41, 467.

[3] *Ber.*, 1929, *62*, 3078.

[4] Cf. Staudinger, Asano, Bondy and Signer, *Ibid.*, 1928, *61*, 2575, on molecular weight of rubber solutions. They also observed delayed crystallization of solvent.

As a result of these observations Freudenberg disputes certain results obtained by Hess in regard to molecular weight determinations of triacetylcellulose in acetic acid. Hess[1] states, however, that determinations are only influenced when the depressions produced by the solute are of a very small order. He attributes the differences in observations by Freudenberg to the following two facts: (1) Freudenberg's acetic acid used had not been purified to such an extent as his solvent; (2) the small under-cooling got by Freudenberg lowers the speed of crystallization, and thereby gives a bigger depression than the actual solute produces.

The following examples illustrate the results obtained in determining the molecular depression constant for acetamide, by Reilly, Wolter, and Donovan. As is usual in molecular weight determinations, the first reading after introducing the substance is generally abnormal, and is omitted in calculating average values:

Acetanilide (low concentration).
0·1974 g. Acetanilide, 16·34 g. Acetamide, concentration 1·208 per cent.

Under-cooling	Reading	Time	Under-cooling	Reading	Time
3·55°	3·191°	5 min.	4·25°	5·550°	5 min.
3·50°	3·190°	4 ,,	4·30°	3·549°	6 ,,
3·61°	3·189°	5 ,,	4·27°	3·551°	5 ,,
Average	3·190°		Average	3·550°	
				− 3·190°	
			Δ =	0·360°	

$$K = \frac{M \times \Delta \times W}{w \times 100} = \frac{135 \times 0{\cdot}360 \times 16{\cdot}34}{0{\cdot}1974 \times 100} = 40{\cdot}2$$

Acetanilide (high concentration).
0·3686 g. Acetanilide, 17·16 g. Acetamide, concentration 2·148 per cent.

Under-cooling	Reading	Time	Under-cooling	Reading	Time
3·29°	3·053°	4 min.	4·09°	3·700°	8 min.
3·23°	3·055°	5 ,,	4·10°	3·702°	9 ,,
3·23°	3·055°	5 ,,	4·06°	3·703°	8 ,,
3·27°	3·056°	4 ,,			
			Average	3·702°	
Average	3·055°			− 3·055°	
			Δ =	0·647°	

$$K = \frac{135 \times 0{\cdot}647 \times 17{\cdot}16}{0{\cdot}3686 \times 100} = 40{\cdot}7$$

Adam's Method. Freezing-point depressions, particularly for very dilute solutions, can be determined very accurately by measuring the difference of temperature between water in equilibrium with ice and solution in equilibrium with ice, using vacuum jacketed vessels. The method has been developed by Adams,[1] Randall and Vanselow [2] and Hovorka and Rodebush.[3] The last author's method is the simplest and will be described here. The apparatus consists of the two silvered Dewar flasks F and G (Fig. 23 (V^3)), which are connected by a thick-walled capillary tube, so that they are maintained at the same degree of vacuum, and which are set in a block of plaster of Paris at the bottom.

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[1] *Ber.*, 1930, *65*, 526.

G is destined to contain ice and water and F ice and solution. The thermocouple B dips into the two flasks and serves to measure the temperature difference. A second single junction thermocouple is connected to the wall at K at one junction, while the other is in F, so that this temperature difference can be measured when necessary; the leads from this thermoelement are carried along the rubber tube C which is connected to the solution vessel E (also set in plaster of Paris). This solution vessel has a tube extending over the top of F for the introduction of solution therein by the application of pressure at C. A cover M of thick paper which has been treated with hot paraffin-wax serves to prevent the introduction of impurities into F and G. The flasks are suspended from the cover N inside the cylindrical copper can K, which is surrounded by the ice in the sheet-metal container H, itself covered with a thick layer of felt. Tube A reaches to the bottom of the Dewar flask F and serves for the withdrawal of solution or for bubbling air. The corresponding tube D serves for air bubbling or for the introduction of water.

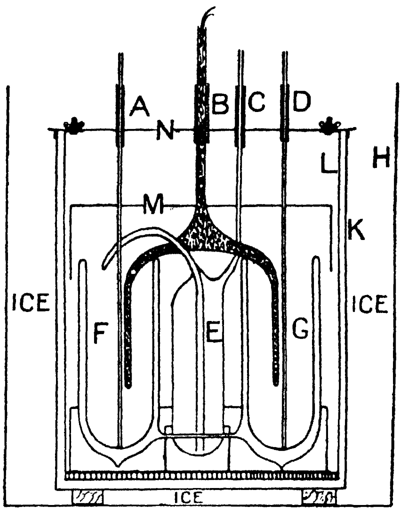

FIG. 23 (V^3)
Rodebush's apparatus

The Thermocouple. This consists of fourteen junctions, each of which is made from three No. 36 D.S.C. constantan wires, and one No. 35 D.S.C. copper wire. The use of three constantan wires in parallel reduces the effects of irregularities in these wires. The wires should be cut to the required lengths and then coated with shellac. About 3 mm. of the ends of the wires are bared and the junctions hard soldered. The solder consists of three parts brass and one part silver, and the flux is anhydrous borax glass. Use small quantities of solder and flux and a small gas jet from a glass tube. Cover the joints with an insulating varnish made by stirring sublimed (or, better, insoluble) sulphur into a solution of crude rubber in benzene and carbon disulphide until the amount reaches 20 to 25 per cent. Dip the junctions in the varnish, dry in the air, and then heat at 140° for 15 hours. Tie the junctions in small bundles with silk thread and then tie the bundles to pieces of thin brass rod to give rigidity. Embed the ends in naphthalene in glass tubes, coat the intermediate portion with melted paraffin-wax (to exclude moisture), and wrap in silk ribbon. Standardize the thermocouple against a standard thermocouple, or by measuring the E.M.F. given between the melting-point of mercury (234·2° K.) and ice (273·1° K.) and the transition point of sodium sulphate (305·5° K.) and ice. It gives about 550 microvolts per degree.

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[1] *J. Amer. Chem. Soc.*, 1915, *37*, 480.

[2] *Ibid.*, 1924, *46*, 2422.

[3] *Ibid.*, 1925, *47*, 1614.

Determination of the Molecular Weight of Potassium Chloride in Aqueous Solution. Prepare an N/100 solution of potassium chloride and place it in the container E ; cool this in a freezing mixture until ice crystals appear : allow the crystals to melt just before putting E in the container L. Clean the two Dewar flasks and wash them with conductivity water before placing in L. Fix the cover N in position together with A, B, C, and D ; and then, through the holes in the sides of L, fill F and G with ice. The ice is cracked in a clean cloth to pieces about 1 ml. in size, then sifted to get rid of the small particles, and washed with conductivity water. Put the assembly in the can H and fill this with crushed ice.

By means of the single element thermocouple determine when the contents of F are within 0·5° of the ice surrounding K, and then suck out the water which has collected at the bottom of F by means of the tube A. Allow a little of the solution from E to flow over the ice in F, and remove this solution from the bottom of F. Repeat this washing of the ice three times, so that the solution will not be diluted by water adhering to the ice. Run in solution from E to fill F. By means of D introduce conductivity water, already cooled to 0°, into G. Air, purified by bubbling through caustic potash and sulphuric acid, is divided into two streams and passed through water and solution respectively in equilibrium with ice, and then at equal rates by way of A and D into F and G ; this stirs the liquids and saturates them with air. After 30 minutes take the first reading of the thermocouple B, bubble the air for a further period of 60 minutes, and again take the reading ; if this does not agree with the former, repeat the bubbling until two successive readings do agree. Then take six readings at intervals of 20 minutes, and use the mean value of the E.M.F. to calculate the temperature difference.

Calculate the molecular weight of the potassium chloride and the fraction ionized.

The Hortvet apparatus described in the chapter on Melting-points may also be employed in molecular weight determinations.

Lowering of the Transition-Point. Lowenherz first investigated the lowering of the transition-point by the addition of foreign substances. He found that the transition-point of sodium sulphate decahydrate into anhydrous sodium sulphate, which is 32·38°, was lowered by such substances as carbamide, dextrose, &c., by amounts which gave a molecular depression of 32·6 when the concentration of the substance is referred to 100 grams of the decahydrate.

Dawson and Jackson prefer to refer the concentration to 100 grams of solution, a change readily calculated from the equation for the reaction, and giving in this case 28·5 for the molecular depression. Other transition-points are magnesium chloride hexahydrate to tetrahydrate, T 116·67°, K = 76; rubidium tartrate dihydrate to anhydrous salt, T 40·41° and K 37·1; sodium bromide dihydrate to anhydrous salt, T 50·7° and K 34·5. The apparatus used is that of Meyerhoffer, in which the Beckmann thermometer bulb is surrounded by a rapidly rotating, perforated, cylindrical Witt stirrer, the speed of which is controlled by a rheostat in the motor circuit. The tube containing the thermometer is surrounded by a wider tube immersed in a thermostat maintained at 3° to 5° below the temperature of the transition-point. About 100 grams of the salt are used and heated about 10° above the transition-point until the transition is complete; the system is then under-cooled about 0·5° below the transition-point, a crystal of the new phase is added and the highest temperature to which the thermometer rises is observed. When the transition has been accurately determined a similar experiment is carried out in which a weighed amount of the solute is added to the weighed amount of solvent and the new transition-point is determined. The concentration of the solution is calculated from the equation; for example, with sodium sulphate, since 100 parts of saturated solution contain 33·4 parts of anhydrous salt, the 'equation' may be written:

$$Na_2SO_410H_2O = 0{\cdot}367Na_2SO_4 + 0{\cdot}100\ (100H_2O.\ 6{\cdot}33Na_2SO_4)$$

therefore 100 parts of decahydrate give 87·3 parts of solution.

The Lowering of Solubility. Nernst has shown that the relative lowering of the solubility of a solute in a solvent by the addition of a foreign substance can be used to determine the molecular weight of the foreign substance. Since

$$\frac{L_0 - L}{L_0} = \frac{n}{N + n}$$

where, for example, L_0 may be the solubility of ether in pure water, L the solubility of ether in the aqueous solution, n is the number of molecules of the foreign substance, and N is the number of molecules of ether. Then if g/M is put for n

$$\frac{(L_0 - L)M}{g} = \frac{L_0}{N + n} \text{ or in dilute solution } = \frac{L_0}{N} = C \text{ and hence}$$

$$M = \frac{g \cdot C}{L_0 - L}$$

This method has been used by St. Tolloczko. He employs a flask holding about 100 ml. and having a neck 15 cm. long and 7 to 8 mm. internal diameter. The flask is fitted with a well-ground-in stopper to make it ether-tight. The neck is graduated in half-millimetres. A few drops of mercury are put in the flask and this is then filled up to a fixed point on the neck, with water saturated with ether which has been purified by shaking with water seven or eight times and two or three times with mercury. Ether is then added so that the ether column is just 60 mm. long. The stopper is inserted and the apparatus is shaken in a thermostat until equilibrium is attained. The length of the ether column is then read accurately to 0·1 mm. with the aid of a lens. A weighed quantity, 0·03 to 0·1 gram, of a substance of known molecular weight, e.g. naphthalene, is added and the flask again shaken in the thermostat. The addition of the naphthalene lowers the solubility of the ether in the water so that the ether column above the water increases in length ; this new length is read off and the data so obtained are used to calculate the constant for the apparatus. As an example, 0·1266 gram of naphthalene altered the length 0·55 cm. ; since the molecular weight of naphthalene is 128,

$$C = \frac{(L_0 - L)M}{g} = \frac{0{\cdot}55 \times 128}{0{\cdot}1266} = 556$$

A similar experiment carried out with benzene, 0·0655 gram, using exactly the same volumes of ether-saturated water and pure ether, gave a change in the length of the ether column of 0·45 cm. Therefore

$$M = C . \frac{g}{L_0 - L} = \frac{556 \times 0{\cdot}0655}{0{\cdot}45} = 81$$

The addition of the mercury promotes the intimate mixture of the two liquids during shaking and a ready separation into two layers on standing.

The Variation of Solubility with Temperature. Van't Hoff's isochore can be applied to the solubility of a substance which is not too soluble in water in order to get a value for the molecular weight. Writing it

$$\frac{\partial \log s}{\partial T} = \frac{Q}{RT^2} \quad \text{or} \quad \frac{1}{s} . \frac{\partial s}{\partial t} = \frac{Q}{RT^2}$$

where s is the solubility and Q the heat of solution per molecule, then

$$Q = \frac{RT^2}{s} . \frac{\Delta s}{\Delta t}$$

and $M = \frac{Q}{q}$ where q is the heat of solution per gram. As an example, van't Hoff gives that 100 grams of water dissolve 2·88 and 4·22 grams of succinic acid at 0° and 8·5°. Hence

$$Q = \frac{2 \times 277^2 \times 1{\cdot}34}{3{\cdot}55 \times 8{\cdot}5} = 6{,}830 \text{ calories per molecule.}$$

The heat of solution per gram is 55, so that the molecular weight becomes

$$M = 6{,}830/55 = 124$$

The Osmotic-pressure Method. Van't Hoff showed that substances in dilute solution are in a state similar to that of a gas, and that if the osmotic pressure of a solution of known concentration can be determined at a known temperature, it is possible to calculate the molecular weight (see below).

If the solute be associated or dissociated in solution, abnormal values for the molecular weight are obtained.

The osmotic pressure of a solution is related to the effect of the solute in lowering the vapour pressure of the solvent, raising the boiling-point, lowering the freezing-point, lowering the transition temperature, and decreasing the solubility of the solvent in another solute. These can therefore all be used to find the molecular weight of the dissolved substance. In a separate section the determination of molecular weights by the osmotic-pressure method is considered.

The Ultra-centrifuge Method. Both the osmotic-pressure method and the ultra-centrifuge method are suitable for the determination of the molecular weight of large molecules, e.g. protein or starch. For an example of this see paper by Svedberg, Carpenter and Carpenter.[1]

Molecular Weight of Large Molecules. When ultra-centrifugal equipment is not available approximate molecular weights of large molecules, e.g. the protein molecule, may be obtained from diffusion and viscosity determination. A detailed discussion has been given to this problem by Svedberg.[2] A short account of the line of argument followed by Svedberg with the formulae as outlined by him is as follows :

If the sedimentation constant s is defined as the rate of settling in unit centrifugal field and reduced to water at 20° as solvent we have for this molecular weight from sedimentation and diffusion [3]

$$M_s = \frac{RT_s}{D(1 - V\rho)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where R is the gas constant, T the absolute temperature, D the diffusion constant, V the partial specific volume of the solute, and ρ the density of the solute.

Molecular weight from equilibrium data is given by the expression [4]

$$M_e = \frac{2RT\,ln(C_2/C_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where C_2 and C_1 mean the concentration at distances x_2 and x_1 from the axis of rotation and ω the angular velocity.

The molar fractional constant (f) may be calculated from the sedimentation constant and the equilibrium molecular weight M_e, or from the diffusion constant by means of the equation [5]

$$f_s = \frac{M_e(1 - V\rho)}{s} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$f_d = \frac{RT}{D} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Experience has shown $f_s = f_d$. For a spherical molecule of the same mass the frictional constant is :

$$f_0 = 6\pi\eta N\left(\frac{3}{4}\cdot\frac{M}{\pi}\cdot\frac{V}{N}\right)^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

For a non-solvated spherical particle and where the dissymmetry of the molecule is roughly that of a stretched ellipsoid of rotation the axial ratio a/b may be calculated by means of the equation : [6]

$$f_0/f = \tfrac{1}{2}\left(\frac{(a^2/b^2)^{\frac{1}{3}}}{(1 - a^2/b^2)^{\frac{1}{2}}}\,ln\,\frac{1 + (1 - a^2/b^2)^{\frac{1}{2}}}{1 - (1 - a^2/b^2)^{\frac{1}{2}}}\right) \quad . \quad . \quad . \quad (6)$$

---

[1] *J. Amer. Chem. Soc.*, 1930, *52*, 141, 270 ; *Ind. Eng. Chem. Anal.*, 1938, *10*, 113.

[2] *Proc. Roy. Soc.*, *B.*, 1939, *127*, 1.

[3] Svedberg, *Kolloidzschr. Zsigmondy-Festschrift*, 1925, *53*, 125 ; *Zeits. physik. Chem.*, 1927, *127*, 51.

[4] *Loc. cit.* ; *Ibid.*, 1926, *121*, 65.

[5] Svedberg, *Zeits. physik. Chem.*, 1927, *127*, 51 ; η = viscosity of solvent.

[6] Gans, *Ann. Phys. Lpz.*, 1928 (4), *86*, 652 ; Perrin, *J. Phys. Radium*, 1934 (7), *5*, 497 ; Herzog, Illig and Kudar, *Zeits. physik. Chem. A*, 1934, *167*, 329.

Kuhn[1] proposed the relationship

$$\frac{\eta - \eta_0}{\eta_0} = 2{\cdot}5\mathrm{G} + \frac{\mathrm{G}}{16}\left(\frac{b}{a}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where η_0 is the viscosity of the solvent, G is the volume of solute per ml. and b/a is the ratio of the long to the short axis of the molecule. According to the deductions of Burgers[2] we have for an elongated ellipsoid of rotation

$$\frac{\eta - \eta_0}{\eta_0} = \mathrm{G}k \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where k is a certain function of the axial ratio of the molecule.

Polson[3] has studied the relation between viscosity and axial ratio for various proteins using axial ratios calculated from values of a/b according to equation (6). It was found that the empirical formula

$$\frac{\eta - \eta_0}{\eta_0} = 4{\cdot}0\mathrm{G} + 0{\cdot}098\mathrm{G}\left(\frac{b}{a}\right)^2 \quad . \quad . \quad . \quad (9)$$

described the behaviour of all the proteins so far investigated. Attached table from Svedberg's paper[4] gives some molecular weights calculated from equations (7), (8), and (9) and comparative figures for ultra-centrifugal molecular weights are also given.

MOLECULAR WEIGHT OF PROTEINS FROM VISCOSITY AND DIFFUSION

Protein	Kuhn	Burgers	Polson	Ultra-centrifugal determination
Gliadin	21,300	13,600	29,600	26,000
Egg albumin	26,800	20,000	41,800	42,100
Lactoglobulin	31,100	22,900	43,700	39,800
Haemoglobin	39,800	30,300	70,300	68,000
Serum albumin	48,000	34,900	71,800	68,500
Serum globulin	134,000	91,300	189,000	158,000
Amandin	224,000	161,000	324,000	329,000
Thyroglobulin	457,000	310,000	642,000	639,000
Homarus haemocyanin . .	530,000	393,000	793,000	777,000
Octopus haemocyanin . .	1,952,000	1,337,000	2,820,000	2,780,000
Helix pomatia haemocyanin .	4,250,000	3,101,000	6,350,000	6,650,000

Svedberg[5] states that the relatively good agreement between the latter and those calculated by means of Polson's equation show that this formula may be of value for the computation of approximate molecular weights in cases where ultra-centrifugal equipment is not available.

Svedberg's Method. The time required to attain the equilibrium, is generally long. Arcihbald[6] has indicated how molecular weights may be determined without waiting for the equilibrium state.

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[1] Illig, *Zeits. physik. Chem. A*, 1932, *62*, 269.

[2] *Second Report on Viscosity and Plasticity Amsterdam*, 1938, p. 113.

[3] *Nature*, 1936, *137*, 740, and unpublished investigations (*see Proc. Roy. Soc. B*, 1939, *127*, 1939, *9*). [4] *Proc. Roy. Soc. B*, 1939, *127*, 10. [5] *Loc. cit.*

[6] *J. Phys. Chem.*, 1947, *51*, 1204.

SECTION 2: MICRO-METHODS

With certain modifications most of the methods described already in this chapter for molecular-weight determinations can be adopted to micro work. In practice, the principal methods used are based on, (1) the raising of the boiling-point; (2) the lowering of the freezing-point; (3) the vaporization process, and (4) the isothermic method. Special applications not already covered will be dealt with here.

Pregl Micro-method

Pregl[1] reduces the amount of solvent used to 1·5 ml. and so carries out determinations of the molecular weight by the Beckmann method with quantities of the solute as small as from 7 to 10 mg. and yet obtains a rise of boiling-point of 0·1° to 0·2° C. The Beckmann thermometer used has a range of 3° C. and is divided into 0·01°; the bulb being smaller than that in the ordinary form does not require so large an amount of solvent to cover it. The liquid is heated by means of a current of hot air which is maintained in a state of uniform motion by a system of four concentric cylinders. The apparatus is shown in perspective in Fig. 24 (V^3) and in section in Fig. 25 (V^3).

The stand has a vertical rod which can be moved up and down and fixed at any desired position. On the rod are fixed two clamps, one for the Beckmann thermometer and one for the neck of the boiling-vessel. By this means the thermometer and boiling-vessel can be moved together without altering their relative positions. A bracket on the foot of the stand supports a brass plate T on which rests the heating-chamber. On the plate is a circular ebonite disc with three feet by which it is fastened to the plate with screws. The brass and ebonite plates have circular holes through which the tube of the micro-burner passes. On top of the ebonite plate are three concentric grooves for supporting the glass cylinders C_2 and C_3, the larger outermost cylinder C_1 being held by the upturned edge of the brass plate. The dimensions of the cylinders are C_1, 14 cm. high by 8·4 cm. diameter; C_2, 12 cm. high by 4·5 cm. diameter; and C_3, 11 cm. high, the upper portion 2·6 cm. diameter and the lower part 3·6 cm. wide. The last has a constricted portion on which rests a circular disk of copper gauze G which serves to heat uniformly the whole cross-section of the rising hot air. A fourth cylinder C_4, 2·6 cm. high by 3·6 cm.wide, fits between the tops of C_2 and C_3; it is covered at the top with a cemented-on mica plate which has a hole in it just large enough to fit the base of the boiling-vessel. C_4 is fixed on the outside of C_3 by means of three strips of asbestos board. The boiling-vessel, as well as the aperture for the thermometer, has one side-arm

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[1] *Quantitative organische Mikroanalyse,* 3rd ed., Sprengler, Berlin, 1930, p. 225, translation by Fyleman of 2nd ed., Churchill, London, 1924; Roch and Daw, *Quantitative Organic Microanalysis of Pregl,* Blakiston Son & Co., Philadelphia, Pa., 1937, p. 242.

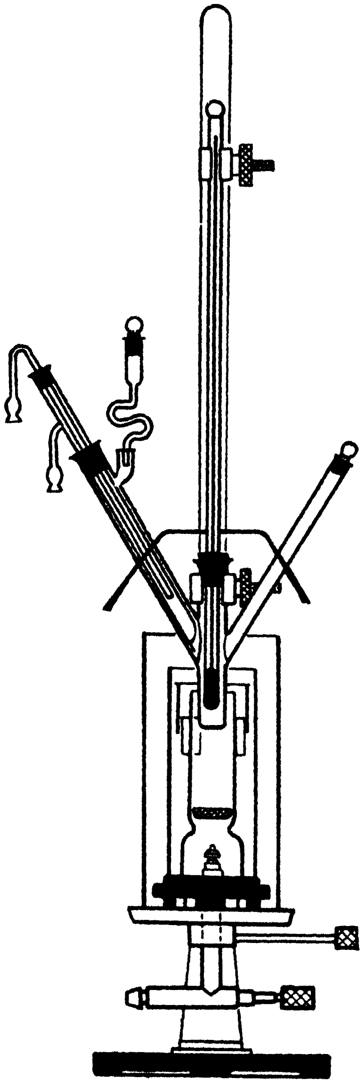

FIG. 24 (V^3)
Pregl micro-boiling-point apparatus
(perspective)

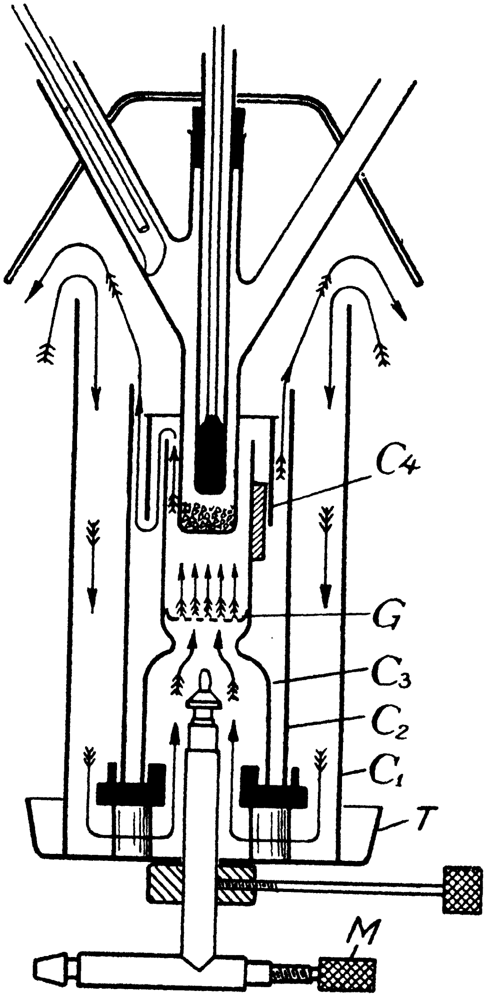

FIG. 25 (V^3)
Pregl micro-boiling-point apparatus
(in section)

13 cm. long serving as a reflux condenser and an arm 10 cm. in length for the addition of the solute; this tube is closed with a glass stopper.

Method of Assembling the Apparatus

The short cylinder C_4 is fixed on C_3 with the aid of the three asbestos strips so that the mica cover is about 1 cm. above the rim of C_3. The flame is then lighted to warm up the glass cylinders. The boiling-tube, previously washed with chromic acid, water and alcohol and dried in warm air, is fixed in its clamp. Some platinum tetrahedra, after ignition, are placed in the boiling-tube and the Beckmann thermometer is fixed by means of a cork so that its bulb almost touches the tetrahedra and it is held in position by its clip. The thermometer is removed, 1·5 ml. of solvent are added from a weight pipette and the thermometer is replaced. Up to this time the base of the boiling-vessel has been above and to one side of the hole in the mica plate; now it is lowered through this hole until the surface of the liquid in the tube is at the level of the mica plate. The tube and C_4 are then pushed downwards a little.

The path of the hot air is then that which is shown by means of the arrows in the diagram. The sheet of celluloid over the top is 20 cm. by 13 cm.; on the longer central line are bored three holes 3·5 cm. apart to fit the three tubes; a slit from each hole to the edge allows the sheet to be put in position and the edges of each slit are then superposed and held in position by a paper clip. Certain precautions are necessary in order to ensure regular boiling. The flame is regulated so that the main tap leading to the micro-burner is fully open, the burner is then turned down till the flame becomes perceptibly smaller. An adjustable pinch-cork is fixed on the rubber tubing, inside which below the pinch-cock is a little cotton wool; this cock is adjusted so as further to reduce the flame which is then made still smaller by the fine adjustment tap on the burner; it was found helpful to have a simple gas pressure regulator in the circuit, one of the bell type used in the carbon-hydrogen determination. A short length of platinum wire is sealed to the tip of the condenser so that the condensed liquid returns in a regular stream instead of in separate drops, since it was found that particularly with solvents of high boiling-point, each drop as it fell back caused a fall in the temperature. About 15 minutes' boiling is generally required before the temperature becomes steady, since this time is required for the cylinders to get heated to a steady state. The temperature readings can then be commenced, using a lens and tapping the tube in the usual way to prevent the mercury from sticking. When the temperature has been steady to 0·002° C. for some minutes the first tablet of solute may be introduced. A special tablet press is used. This consists of three parts, a round base-plate 4·5 cm. across with a flat polished surface on one side and a large cylindrical opening on the lower side. On this rests a second steel plate of the same diameter and 0·9 cm. thick and with a central smooth-walled hole which is 2 mm. in diameter tapered outwards at the top. The solid is placed in this hole and is pressed over with the compressor which just fits the hole; the bottom plate is then inverted and a sharp blow on the compressor forces the tablet out into the hollowed-out cylinder in the base. The tablets should weigh about 7 or at most 10 mg. and are weighed in weighing tubes on the microbalance to 0·01 mg.

A small charging tube made of glass is used for the introduction of the tablet, it is 4 mm. in diameter, 15 mm. long, has a small depression made at one point and is attached to a glass handle 15 cm. long. The tube is held with the depression downwards and with the tablet contained in the depression; it is inserted as far as possible down the side-tube of the boiling-vessel and is then rotated so that the tablet falls out. As the tablet dissolves the temperature rises at first gradually and then more rapidly before it finally becomes constant; the second tablet is then introduced in the same way. Generally 12 to 15 mg. of material can be recovered which is enough for all the elements to be determined. Pregl gives examples showing an accuracy of about 2 per cent.

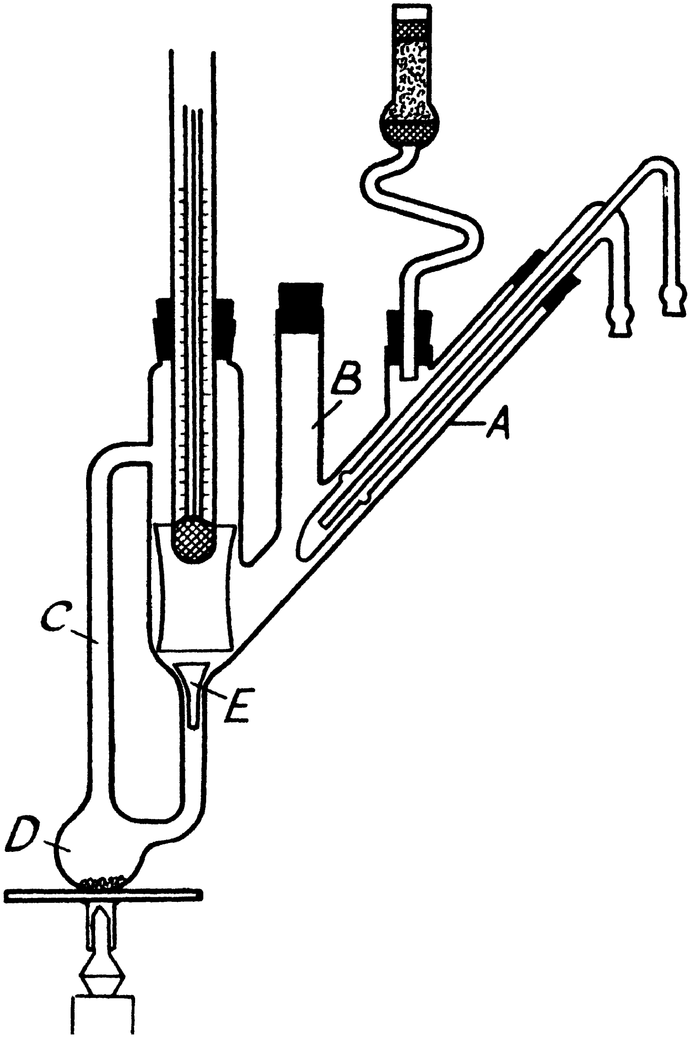

FIG. 26 (V^3)
Rieche's molecular weight apparatus

Rieche's Molecular Weight Apparatus. This apparatus first devised by Rieche [1] and later modified,[2] is illustrated in Fig. 26 (V^3). Here *D* is the boiling-chamber in which are some platinum tetrahedra to aid regular ebullition, *C* is the vertical tube through which rises the mixture of vapour and liquid which spills over the bulb of a micro-Beckmann thermometer similar to that used in Pregl's apparatus. The bulb of the thermometer is surrounded by the glass cylinder shown and the overflow from this passes to the tube containing the valve *C*. The liquid flowing from the condenser *A* passes to the same tube, and when sufficient liquid has collected here its buoyancy raises the valve and allows it to pass back into *D*. When the apparatus has reached a steady state the return flow at *C* is practically continuous. The vertical tube *B* makes it easy to introduce the solute which is readily washed down by the solvent refluxing from the condenser.

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[1] *Ber.*, 1926, *59*, 218, and *Chem. Zeit.*, 1928, *52*, 923.
[2] *Mikrochemie*, 1933, *12*, 129.

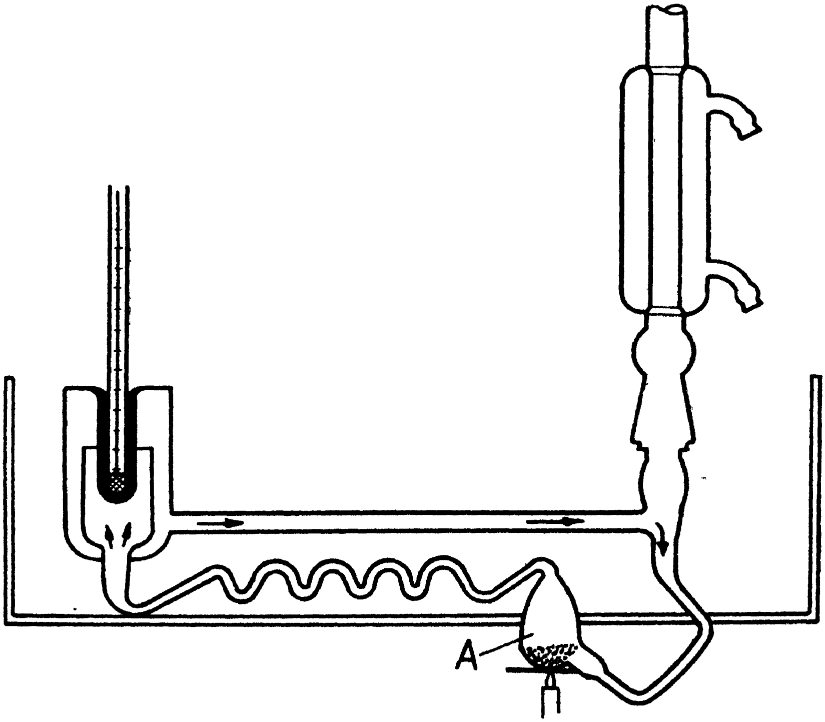

FIG. 27 (V^3)
Semi-micro-boiling-point apparatus

The boiling-bulb is heated by a micro-burner similar to that used by Pregl and protected from draughts by a glass chimney. The bottom and sides of the apparatus are also protected from draughts by a box of asbestos board: this is a precaution specially important in the case of solvents of low boiling-point. 4 ml. of solvent are used and pellets of solute weighing about 20 mg.; the method of procedure and the precautions observed follow closely Pregl's method.

Sucharda and Bobranski's Semi-micro-method is described in their book.[1] Fig. 27 (V^3) shows a diagram of the apparatus: here the boiling-vessel which is pear-shaped, 3·5 cm. high and 1·7 cm. wide, is shown at A. Instead of the usual platinum tetrahedra splinters of glass are fused to the inside of the bottom to aid in the regular evolution of bubbles of vapour. From the top of the pear the sinuous horizontal tube some 9 cm. long and 0·5 cm. bore leads to the thermometer chamber. The thermometer bulb lies in the well in the outer cup ; this well is 4·5 cm. deep and contains 3 to 4 ml. of mercury to give good thermal contact. The inner cylinder is 4 cm. high and 2 cm. wide, while the outer is 6·5 cm. high and 2·5 cm. in diameter. The liquid which flows over the rim of the inner cylinder flows along the wider (0·8 cm.) tube to the narrow (0·3 cm.) tube, by which it returns to the bottom of the pear-shaped bulb. The vertical condenser is about 20 cm. long and is attached by a ground-in joint. Here, again, an asbestos-board box is used as a protection against draught and as heater is used a micro-burner with a chimney. A piece of wire gauze is placed above the flame, but it is sometimes necessary to apply a direct flame to the glass in order to set up free circulation of the liquid at the start : once this has been secured the micro-burner flame is adjusted until the liquid just flows over the rim of the inner cylinder. In this case 5 ml. of solvent are used and about 25 mg. of solute. Pellets may be dropped down the vertical condenser, but in the case of solids which do not readily compress into pellets the micro-burner is removed for 5 minutes, the condenser is taken out and the solid added through the ground-glass joint ; the condenser is replaced at once and the heating restarted.

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[1] Braunschweig, 1929.

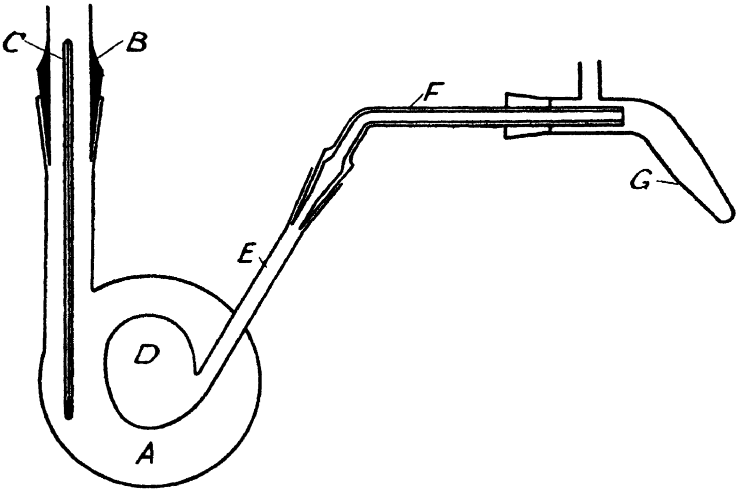

FIG. 28 (V^3)
Boiling-point apparatus (for high temperatures)

The High Temperature Apparatus.[1] This is made of Pyrex glass and can be used for temperatures up to 330°. As shown in Fig. 28 (V^3) the vaporizer, D, of about 15 ml. capacity is sealed into the 350-ml. flask, A ; the stem, E, of the vaporizer is 15 cm. long and 6 mm. internal diameter and terminates in a ground-glass joint. It is sealed in at an angle of 45° near the base of the bulb B. The vertical side-tube of the flask A is 8 cm. long and 2 cm. in diameter. It has a ground-glass joint at the end which will take either a Liebig water condenser or an air condenser according to the boiling-point of the liquid in the bath. The thermometer C is hung by a wire extending through the tube of the condenser. Into the stem from the vaporizer is jointed the capillary outlet 2 mm. internal diameter and with arms 5 and 10 cm. long. On E and F are glass hooks by which springs are attachable to hold the joint. The centrifuge tube G is bent as shown and has a side-arm which can be connected to a pump.

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[1] Niederl and others, *Mikrochemie*, 1932, *11*, 237, and 1932, *11*, 251.

Procedure. Ordinary liquids are weighed in pipettes like those used in the low-temperature apparatus: the solid rod as well as the capillary thread are cut before introduction into the vaporizer because if the glass is too long it will not be able to pass the bend into the bulb. For viscous liquids capillaries 8 cm. long and 1·5 mm. internal diameter are used. After weighing, the end of the capillary is placed in the liquid which is allowed to rise to a height of 3 or 4 mm. (5 to 8 mg.), the outside is wiped and the tube weighed. The tube is then cut about 2 mm. away from the liquid meniscus and the part containing the liquid is put in the vaporizer. With solids a similar procedure is followed after melting the solid on a watch-glass or in a narrow tube. If the solid sublimes it has to be placed in a capillary closed at one end (2 mm. bore). The vaporizer and tubes are filled with mercury after the tube containing the substance has been added; the manner of filling is similar to that previously described. Liquid is added to the bath so as to cover about two-thirds of the inner bulb and pieces of porous porcelain are added to help in regular ebullition. The apparatus is then clamped to the stand, the condenser attached and the thermometer lowered into position. The apparatus is now allowed to stand until temperature equilibrium is reached and any necessary adjustment of the mercury is made so that it reaches to the end of the tube F and there is none in the receiver G. The initial temperature T_1 having been noted, the bath is quickly heated up to the boiling-point of its liquid: this heating may be done with a free flame or an oil, sand or Wood's metal bath. Once the bath A begins to boil it is kept gently boiling for 2 minutes, the temperature T_2 is read, heating is stopped and the apparatus is allowed to cool. The mercury which has been discovered can then be weighed to 0·1 gm. The correction for the expansion of the glass, mercury, &c., can be determined by a blank experiment as with the other apparatus. The object of the side-tube on G is so that the whole operation can be carried out at a constant pressure which is less than atmospheric if it is so desired.[1]

Barger's Method

This technique is an application of an observation by the botanist Errara. He found that the volumes of hanging droplets of solutions of salts in an enclosed system increased, while those containing solvent alone decreased. As worked out by Barger the method depends on the fact that equimolecular solutions in a given solvent will have their vapour pressures lowered by the same amount and so will have the same vapour pressure. If two solutions, not having the same vapour pressure, are enclosed in the same vessel, distillation of solvent will take place from that having the lower molecular concentration to that having the higher. If the vapour pressures are the same, no distillation will occur, so that this can be used as a criterion of equality of molecular concentration. In this case if the molecular concentration of one solution and the weight concentration of the second are known, the molecular weight of the second solute can be calculated.[1]

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[1] Niederl and Niederl, *Organic Quantitative Micro-Analysis*, 2nd ed., 1942, pp. 210–38, John Wiley & Sons, N.Y. There is an exceptionally good section on the 'Determination of Molecular Weights' by (1) Ebullioscopic methods; (2) Cryoscopic methods; (3) Vaporimetric methods; and (4) Isothermic methods. The various methods are critically compared and an excellent summary of the related literature is also given.

To see whether distillation takes place short lengths of the two solutions are sealed in a capillary tube, the two solutions being separated by an air bubble. The lengths of the columns of solution are then measured under the microscope from hour to hour. A solution of known concentration of the substance under examination is compared in this way with a series of solutions of a standard substance of known molecular weight.

The method has the advantage that the solvent need not be specially pure, and that very minute quantities of the solute are necessary. As standards Barger used cane sugar in water solution and benzil or azobenzene in organic solvents. When the substance examined is colourless it prevents confusion if a coloured substance like azobenzene is used as comparison solute.

Example of the Determination of the Molecular Weight of Naphthalene with Ethyl Acetate as Solvent and Azobenzene as Comparison Substance. *Preparation of Solutions.* An approximate idea of the molecular weight is generally available and a convenient concentration to use is about 0·2 molar. In this case that will be about 128 grams in 5 litres or 0·128 gram in 5 ml. Weigh a small bottle and add about 0·13 gram of naphthalene and weigh again to get the exact weight used. Calculate what volume of ethyl acetate is required to give, with the weight of solute found, a solution of the required concentration, and add this volume from a graduated pipette or a 10-ml. burette. Weigh the bottle again and get the weight concentration of the solution.

Next prepare a series of solutions of azobenzene, having 0·20 M as the central concentration; for example, they might be 0·16 M, 0·17 M, . . . 0·24 M: since the molecular weight is 182, 0·364 gram will be required for 10 ml. of solution of 0·20 M concentration. The simplest method is to weigh about 0·3 gram into each of nine bottles and then to calculate what volume of solvent is required in each case: add this volume from the 10 ml. burette and weigh to get the exact molar concentration.

Preparation of Capillaries. Take soft glass tubing of 0·5 in. bore and draw it out into capillaries about 2 metres long; the external diameter should be 0·5 to 1·2 mm. Lengths of 20 to 30 cm. are then cut, care being taken that the ends are cut off square. One end of a capillary is closed with the index finger, and the other end is placed in the first comparison solution: release slightly the pressure on the finger and let a length of about 5 cm. of solution enter. Close the end with the finger and turn the tube with the open end uppermost, and by slightly releasing the finger let in a 3-cm. air bubble.

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[1] *J. Chem. Soc. Proc.*, 1903, *19*, 121; *Trans.*, 1904, p. 286; *Ber.*, 1904, *37*, 1754.

Wipe the outside of the tube and with the finger pressed on the closed end lower the open end into the solution to be examined, and allow 5 cm. of this to enter: draw this into the tube so as to leave about 3 cm. free. Seal the comparison end and draw out the other end to a very fine capillary, using a flame 3 mm. high; break this off till a length of 2 cm. remains; this is then melted in the flame. Then draw out the comparison end and break off the tip; similarly with the finger-nail break off the tip at the solution end and, by tilting the tube, let this run down until the fine point of the capillary is filled, and then seal this tip with the very small flame, and then the other tip. The liquid under examination thus extends right to the end of the tube, so that any increase or decrease in volume will be shown at one end only. A glass strip 17 cm. long and 2 cm. wide is taken and a reference line marked on it in such a position that when the capillaries are attached to the strip, the free ends of the columns of solution of the substance under test are near the line. The line may consist of a black hair or a strip of tinfoil fastened across the glass with Canada balsam. The series of tubes which have been prepared are now placed on the glass strip in the correct order, and so that the free end of the drop to be measured is within half a millimetre of the reference line; they are then fixed in position with Canada balsam. The glass strip is now placed in a glass dish made from a strip of glass 20 cm. by 4, by fastening four glass rods cut to size along the edges by means of paraffin-wax. The dish is filled with water, which not only keeps the temperature steady, but also improves the optical definition. The dish is placed on the stage of the microscope: using a magnification of about 100 and a micrometer eye-piece, after 10 minutes the first reading is taken; the distance of each meniscus of the solution under test is measured from the reference mark. After from 3 to 12 hours these readings are repeated; at one end of the series the column of test solution will be found to increase in length while at the other they decrease: so it will be possible to find two neighbouring tubes one of which shows a slight increase and the next a decrease: the molecular concentration of the substance under test is then between those of the corresponding comparison solutions. If desired, a further series of tubes between these limits can be set up and the exact point narrowed down still further: an approximate estimate of this point can be made from the amounts of the changes in length in the two cases; this can best be seen by an example: the first line gives the normality of the comparison solution, the second line the series of readings on the micrometer scale taken at the start, the third line the micrometer readings after 12 hours, and the last line the change in the reading.

0·1 M	0·3 M	0·4 M	0·5 M	0·7 M
– 40	– 49	– 38	– 37	– 21
+ 100	0	– 21	– 56	– 90
+ 140	+ 49	+ 17	– 19	– 69

The normality of the naphthalene solution obviously lies between 0·4 and 0·5, and the gain of 17 on one side and the loss of 19 on the other show that the value will not be very far from 0·45. A second series then gave the following results :

0·42 M	0·44 M	0·46 M	0·48 M
− 25	− 30	− 17	+ 1
− 1	− 26	− 17	− 24
+ 24	+ 4	0	− 25

this gives the normality of the solution as 0·46 and since it was made up to contain 57·6 grams per litre of naphthalene we have that

0·46 M solution contains 57·6 grams per litre, therefore

1·00 M solution contains 57·6/0·46 grams per litre = 125 (theory 128)

Modified Methods

Various adaptations of Barger's method have been suggested. Among these the following may be noted : Rast [1] used one drop of each of two solutions and measured the movement of the gas bubble which divided the two solutions. His concentrations varied from 0·2 to 1 M. Fredrich [2] used lower concentrations and worked with two drops and avoided the end air-spaces. Spies [3] has simplified the technique in the preparation of the capillary tube. In the ordinary Rast method the drop of the standard solution and those of the test solutions are introduced into a capillary with 3–4 mm. air space separating them and the tube is heated and closed on the right and drawn out 2 cm. to hairbreadth on the left. In the modifications of Spies, instead of breaking off the left end at the end of the hair, it is allowed to remain, leaving a funnel-shaped reservoir as in Fig. 29 (V^3).

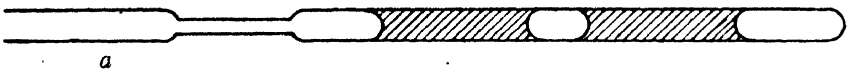

FIG. 29 (V^3)
Spies' form of capillary tube

The right end is now broken and the tube tilted so that the liquid flows back through the hair capillary to the position *a*. The tube is then drawn out on the right to hairbreadth for 2 ml., broken at the end of this ' hair ' and tilted so that the liquid runs into and fills it, whereupon it is sealed by carefully touching it in a micro-flame. Some of the liquid should remain in the funnel on the left so that the hair-wide tube on the left is still filled. This funnel is then broken off and the end of the ' hair ' passed rapidly through a micro-flame to expel a small portion of the solution before sealing as on the right. A 5 × 17 ml. glass plate with a line etched through the centre parallel to the short side replaces the 1–2 × 17 ml. plate used by Rast. The etched line takes the place of the ' hair ' covered with Canada balsam. When it stands in water, balsam gradually becomes opaque and must be replaced daily.

Schwarz [4] instead of measuring the volume of the drops determined the amount of vapour distilled. Berl and Hafter [1] employed a U-shaped capillary.

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[1] *Ber.*, 1921, *54*, 1979.

[2] *Mikrochemie*, 1928, *6*, 97.

[3] Spies, *J. Amer. Chem. Soc.*, 1933, *55*, 250.

[4] *Monatsh.*, 1929, *53*, 926.

Improved Isothermic Method

Barger's method is open to the objections that there may be some mixing of the little drops either during the filling or on standing and that the length of the drops is very short.

Niederl and Levy [2] have modified the method so as to avoid these difficulties by placing each liquid in a separate capillary and enclosing one standard and one unknown solution in a closed tube which in the case of solvents boiling about 70° C. may be evacuated. The capillaries are 10 to 12 cm. long and 1·5 mm. in diameter : it is most important that they should be of uniform diameter owing to the effect which a change in the radius of curvature of the meniscus has on the vapour pressure of a liquid.

A glass plate 12 cm. by 4 cm. by 2 mm. has five parallel reference lines 3 mm. apart marked across it ; the lines may be marked I to V. A low-power microscope is used, object glass 4·6 × and eyepiece 7 ×. The eyepiece has a micrometer scale marked 0 to 50, the 50 divisions cover 1·5 mm., i.e. half the distance between two lines on the plate.

Solvents. Acetone or chloroform are used at atmospheric pressure. Alcohol, benzene, pyridene, and other solvents having a somewhat higher boiling-point are used under reduced pressure.

Standard Solutions. A series of these, preferably of a coloured solute, is prepared on a macro scale starting say with 250 ml. of 2 M solution and preparing by suitable dilution with solvent 25 ml. of 0·15, 0·1375, 0·125, 0·1125, 0·10, 0·0875, 0·075, 0·0625, and 0·05 M. The sample solution may be prepared by weighing 4 to 6 mg. in a weighing-tube which is then placed in a glass-stoppered weighing-bottle which is weighed on an ordinary balance to 1 mg. By means of a dropping-pipette about 0·5 ml. of the solvent is added (necessarily the solvent is the same as used in making the standard solution). The weighing is repeated to get the weight of solvent used and by dividing by its density we get the volume of the solution. Obviously if sufficient solute is available we may work on a larger scale with advantage.

The capillaries are filled in sets of four : first the unknown solution X. A capillary is taken and 8 cm. of solution drawn in by suction ; the dry end is sealed in the micro-burner and the solution is transferred to this end with the aid of the centrifuge. Three more capillaries are filled in the same way, trying to get as near as may be the same length of solution in each case. With very volatile solutes the end of the capillary may first be drawn out still finer.

Four standards (S) are now prepared in exactly the same way, for example, from the 0·2, 0·15, 0·10 and 0·05 M solutions ; if the solvent is colourless a minute coloured glass bead is put in each tube. The unknowns and the standards are then paired off so as to get each pair with nearly the same length of liquid.

Each pair (X and S) is then put in a glass tube sealed at one end and 15 cm. long by 5 mm. internal diameter. The sealed ends are at the bottom of this tube and the capillaries are fixed in position by a plug of glass wool pushed down behind them so as to be between their open ends and the liquid meniscus. With the more volatile solvents, i.e. those boiling below 70° C., the tube is sealed at atmospheric pressure but to prevent undue evaporation during this process the closed ends of the tubes are put in ice water for 10 minutes. After removing and drying, the outer tube is sealed as near as possible to the open ends of the capillaries. With solvents boiling above 70° C., after the first cooling the wall of the outer tube is softened and drawn out to a capillary. The tube is put back in the ice water and when it has cooled is attached to a water pump and evacuated ; without stopping the pump the capillary is heated whereupon the walls collapse and the tube is sealed : a mark to indicate which standard solution is contained is made on the outside of the glass.

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[1] *Ann.*, 1930, *478*, 235.

[2] *Science*, 1940, *92*, 225.

The tube is placed on the glass plate in such a position that each of the meniscuses lies between the transverse marks on the glass plate and is fixed in this position with a piece of surgical adhesive tape applied at each end. More than one tube may be mounted on each plate.

Reading the Position of the Meniscus

The range of the scale in the eyepiece is 1·5 mm. while the distance between two reference lines is 3 mm. so that when a meniscus lies between two reference lines its distance from both cannot be measured ; however, its position is fixed if its distance from either is measured so that we can measure either the length of the liquid columns from the base of the meniscus to the reference line or the length of the air columns, again from the base of the meniscus to the reference line, whichever is possible.

The plate is placed on the stage so that the liquid is on the left and the meniscus of the standard solution is brought into focus; suppose that the reference line crossing the liquid is the nearer to the meniscus : move the plate until the zero of the scale coincides with the base of the meniscus then focus on the reference line and take the scale reading. The length of an air column is measured in the same way, except that the plate is moved so that the 50 mark on the scale coincides with the base of the meniscus and the length is of course 50 minus the scale reading of the reference line. Readings are made of all the tubes at the start and then at intervals of 1 day and then 3 days.

Some readings given by Niederl are :

SCALE READINGS

Concn. of standard	Standard solution				Unknown			
	at start		after 24 hrs.		at start		after 24 hrs.	
0·050 M	Liq. II	40	L II	10	L III	10	L III	26
0·075 M	Air III	10	A III	30	A IV	24	A IV	10
0·100 M	L II	30	L II	20	A III	30	A III	20
0·125 M	A IV	7	L IV	7	L III	10	A III	10
0·150 M	A III	20	A III	4	L II	11	A II	10

The changes in length were:

	Standard	Unknown
0·050 M	− 30	+ 16
0·075 M	− 20	+ 14
0·100 M	− 10	+ 10
0·125 M	+ 14	− 20
0·150 M	+ 16	− 30

These figures indicate that equivalence is somewhere in the neighbourhood of the 0·100 M solution and it would be well to try with the series of standards near this point, viz. 0·125, 0·1125, 0·10, 0·0875, and 0·075 M.

In practice various cases may be encountered: It is very unusual to come across a pair (S and X) which both show the same decrease in volume while the other members of the series all show differences. Cases of reversal like the one for which figures are given indicate the approximate molarity of the unknown; here we find the less-concentrated standards losing and the unknown gaining at one end of the series and at the other end the standard gains at the expense of the unknown. Sometimes all the solutions decrease in volume (particularly in earlier observations) then the observations should be continued until a definite reversal is obtained. It may be desirable to repeat the determination with different standards.

Rast Method and Modifications

In 1912 attention was drawn to the application of camphor for molecular weight determination.[1] Later it was shown that with an ordinary thermometer it could be employed for such work.[2] And a figure 498 was deduced for the molecular lowering of camphor. This figure is much higher than that afterwards employed by Rast, but it is in good agreement with an indirect calculation. From van't Hoff's relation the latent heat of fusion of camphor is 8·24 calories. Calculated from the vapour pressure determination of camphor by Ramsay and Young, combined with a knowledge of the specific volumes of camphor in the liquid and solid states, a value of the latent heat of fusion is obtained, identical with that deduced from van't Hoff's equation.

Since camphor melts at 174° the method is not applicable to substances which decompose lower than 180°. Again, melted camphor contains both the keto and enol forms, so that the substance used must be soluble in camphor but at the same time must not react with either form.

The camphor method of Rast,[3] which has been widely used in microwork in recent years, depends on the extraordinary great freezing-point depression constant of camphor (40° for one gram molecule of dissolved substance in 1 kg. camphor), which allows the molecular weight of a substance to be determined from a simple observation of the 'mixed' melting-point of the substance and camphor, taken with an ordinary accurate thermometer. With substances of fair solubility in molten camphor (e.g.

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[1] Jouniaux, *Bull. Soc. Chim.*, 1912 [4], *11*, 546; also see Le Fèvre (*Nature*, 1930).
[2] *Ibid.*, p. 722.
[3] *Ber.*, 1921, *55*, 1051.

10 per cent) and average molecular weights, a freezing-point depression of about 8° to 20° is obtained : but, as has been noted by Pregl, the method is obviously limited for many substances by their low solubility in camphor.

Ten mg. of the substance under examination are mixed with 100 mg. of camphor. The melted mixture, when clear, is then allowed to solidify. The next operation consists in breaking up this material, and part of it is placed in a small melting-point tube as in the carrying out of an ordinary melting-point determination (*see* the chapter on this subject), and the melting-point determined in the usual way. The difference from the original camphor is the '*depression*'. The method is claimed to be accurate to within 5 per cent. When more of the substance is available the following method may be used in which a determination of the Freezing-point Depression Constant precedes the actual Molecular Weight Determination : this is desirable because the value found by slightly different technique is somewhat variable, while an individual observer can get very consistent results by following exactly his own procedure on each occasion. Rather larger capillary tubes (10 cm. long by 2–3 mm. diameter) are used. Some pure camphor is ground to powder with a spatula on an unglazed porcelain plate and is put into the capillary and pressed down with a glass rod so that the column is about 15 mm. high. The camphor is melted, using the ordinary melting-point apparatus, to give a clear liquid and the temperature of the bath is then allowed to fall till solidification is complete. The heating of the bath is resumed at the rate of not more than 1° per minute and the temperature taken when the last trace of crystals disappears. The determination is repeated to confirm the accuracy of the result. The next step is to determine the F.P. depression constant using some substance such as naphthalene ($C_{10}H_8$. M.W.128). A clean specimen tube is weighed, about 0·2 gram of naphthalene put in and the tube reweighed : then about 2 grams of finely divided camphor is added and the tube and its contents again weighed. A loosely fitting cork is put in the tube which is heated over a small flame so as to melt the contents at as low a temperature as possible. While cooling, the contents are swirled round to keep the mixture homogeneous. The solid contents of the tube are removed with a spatula, or if necessary the tube is broken and the contents are ground up in a mortar : the material so obtained is then used for a melting-point determination carried out in exactly the same manner as that for the camphor alone. With the mixture before the melting-point is reached an appearance is seen first like that of melting ice and then of a turbid liquid. If this is carefully examined with a lens, a sharp crystalline skeleton can be distinguished, which at first permeates the whole mass and which, on slowly heating, disappears from the top downwards. The disappearance of the last trace of crystals from the bottom is to be taken as the melting-point of the mixture. From these results the F.P. depression constant is calculated. Finally the experiment is repeated in each detail as for the naphthalene, but using the substance for which the molecular weight is required. With an unknown substance a fresh determination would be made using a new mixture containing a higher percentage of camphor to make sure that the whole of the solute was in solution. The camphor method has been modified by Reilly and Pyne [1] so as to enable small depressions to be estimated with accuracy, and so permit of the determination of molecular weights from quite small depressions of freezing-point. Though devised to meet a particular difficulty presented by the pigment produced by *Chromo-bacterium violaceum*, it is of general application, and it will be described here in detail.

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[1] *Sci. Proc. Roy. Dub. Soc.*, 1927, *18*, 42, 489.

The micro-method of Reilly and Pyne depends on the preparation of cooling curves for slowly cooling camphor before and after the addition of the substance whose molecular weight is to be determined. As only small amounts of camphor are employed, the thermometer should be small-bulbed. An Anschütz thermometer, graduated in fifths of a degree, and capable of being read by means of a mounted lens to one-fiftieth of a degree Centigrade, is quite suitable. The temperatures may also be obtained by means of a thermocouple. The procedure is as follows :

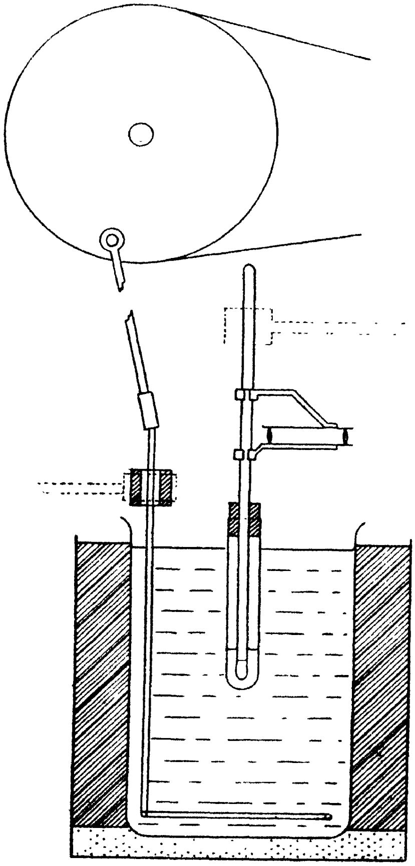

FIG. 30 (V^3)
The micro-freezing-point apparatus of Reilly and Pyne

0·3–0·7 gram camphor (Kahlbaum's, further purified by sublimation) is introduced into a small, fairly strong test tube (10 mm. × 60 mm.), which is closed by a well-fitting cork, carrying the thermometer. The tube is then immersed up to 2–3 mm. from the bottom of the cork in glycerine contained in a 400-ml. beaker, which forms the heating-bath. It is necessary to close completely the test tube in this manner, and almost totally immerse it in the bath, in order to prevent sublimation of the heated camphor. With recording of temperature changes by a thermocouple even smaller amounts of substance may be used. The heating-beaker is contained in a second vessel (an ordinary tin container serves well), the bottom of which is covered with a layer of sand : and the annular space between the two is filled with loose asbestos. The object of this insulation is to enable cooling to take place sufficiently slowly to give a cooling curve with a well-defined melting-point flattening. A motor-driven stirrer is used, to prevent inequalities of temperature in the glycerine, and thus ensure a perfectly uniform rate of cooling. When the test tube containing the camphor is in position, the bath is heated to about 180° by a Meker burner. As soon as the camphor melts, the thermometer is lowered or adjusted through the cork, so that its bulb is completely covered by the camphor, and centrally positioned. The

Meker is then replaced by an ordinary Bunsen or Argand burner, turned down fairly low– the size of the flame being so adjusted that the rate of cooling of the camphor does not exceed 0·8° per minute. A rate of 0·4°–0·8° per minute is the most favourable. The motor stirrer is then set going, and, after the temperature has fallen to 178°, it is read every quarter of a minute by means of an eyepiece mounted on the thermometer. (*See* Fig. 30 (V^3). It is unnecessary to plot the readings to determine the melting-point. The temperature is always found to remain steady for two or three readings at some point, which is taken to be the melting-point. Sometimes a slight rise in temperature occurs, and then the highest point reached is taken. It is advisable, however, to take readings every quarter of a minute, and not to depend on observation alone to determine the point at which the temperature remains steady, for the latent heat of the small amount of camphor used only produces a very momentary effect on the rate of cooling, which might easily be missed.

While the camphor is still hot, or after it has been remelted if necessary, the thermometer is taken out, allowed to cool, and any camphor which has sublimed around the cork is removed. 2–5 mg. of the substance whose molecular weight is required are compressed to form a small pellet (or a single crystal may be used), weighed on the micro-balance, and dropped into the tube. The stopper and the thermometer are inserted once more, and the tube heated up again in the glycerine bath. As soon as the camphor melts, the test tube is gently shaken to ensure proper solution of the added substance, the thermometer properly adjusted in the melt, and the cooling curve determined as before. After the estimation, the cork and thermometer are taken out, and the tube is freed from camphor which has sublimed near the cork, and then weighed. The weight of camphor in which the substance was dissolved at the moment of the estimation can thus be determined.

The following are examples of some molecular weight determinations made in this manner by Reilly and Pyne: [1]

Δ = Depression of freezing-point.
M = Molecular weight.

Mol. coeff. of lowering (for camphor) = 40° (1 gram-mol. in 1 kg.).

1. Acetanilide, 2·54 mg. in 432 mg. camphor.
   $\Delta = 1{\cdot}80^\circ$
   Found M = 129. Theor. M = 135.
2. Strychnine, 5·11 mg. in 524 mg. camphor.
   $\Delta = 1{\cdot}18^\circ$.
   Found M = 331. Theor. M = 334.
3. Palmitic Acid, 5·23 mg. in 689 mg. camphor.
   $\Delta = 1{\cdot}18^\circ$.
   Found M = 257. Theor. M = 256.
4. *o*-Benzoyl di-*p*-tolyl oxide 3·814 mg. in 293 mg. camphor.
   $\Delta = 1{\cdot}66^\circ$.
   Found M = 314. Theor. M = 302.

The apparatus described is constructed from the simplest materials. Its use, of course, involves that of a micro-balance, since it is a micro-method. No doubt it could be made still more sensitive. It has been made available for use with even smaller amounts of substances, and those which are less soluble, by some further slight changes. By employing, e.g. a small-bulb thermometer graduated in one-tenths of a degree, and a short-focus table cathetometer for reading the temperature, its sensitiveness is increased four-fold ; the use of a thermocouple increases the sensitiveness still more. Electrical heating can also be used, and it gives both a quicker heating up and a more easily controlled cooling than gas.

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[1] *Sci. Proc. Roy. Dub. Soc.*, 1927, *18*, 42, 489.

The most important manipulative matter is the proper adjustment of the rate of cooling. If this is too rapid, the latent heat evolved on the solidification of the camphor is insufficient to counterbalance it, and a steady fall of temperature ensues, in which no point of arrest can be detected. A rate of fall of about 0·8°, or less, per minute has been found to give satisfactory results. Fig. 31 (V^3) shows two cooling curves which illustrate this fact. In one curve the rate of cooling was about 1·6° per minute ; in the other 0·85° per minute. The second curve shows a marked flattening at one section which denotes the freezing-point of the camphor, while the first shows a continuous fall of temperature without any break. Besides ensuring that the rate of cooling is low enough, the only other point which needs attention is the very obvious, but important, one of inserting the thermometer so that the bulb is completely surrounded by camphor, and equidistant from the walls of the tube. Neglect of this precaution leads to the production of a cooling curve of type 1, in which no clearly defined melting-point is discernible.

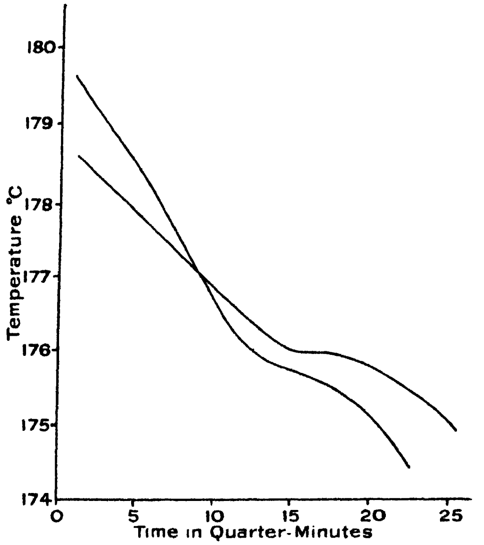

FIG. 31 (V^3)

(Cooling curves for camphor (at different rates)

Dupont [1] states that camphenylone obtained by the oxidation of camphene by nitrogen peroxide is a good cryoscopic solvent. The melting-point is about 35° and the constant 600.

Modified Apparatus. A modification of the apparatus of Reilly and Pyne has been devised by Gee for the determination of the molecular weight of rubber and related substances. An account of this work is given in the Faraday Society Proceedings and in publication No. 15 of the British Rubber Producers Research Association.[2]

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[1] *Bull. Soc. Chim.*, 1933, 1159.

[2] *Trans. Faraday Soc.*, 1940, 1171 ; 1941, 38. The authors are indebted to Mr. G. Gee and to the Rubber Producers' Research Association for permission to give an account of this and to reproduce Figs. 32 (V^3) and 33 (V^3).

The Rast method as applied to rubber gives somewhat variable results in the hands of different workers, but there is general agreement in indicating a molecular weight of the order of 1 per cent of that obtained from osmotic data. A number of objections to the method have been raised [1] but they are concerned only with relatively minor corrections and thus do not affect the main problem, which is that of the order of magnitude of the molecular weight. Similarly low values of molecular weight have been calculated from the freezing-point depression in menthol solutions, but it has been shown that the freezing-point of menthol itself varies with the rate of crystallization by an amount comparable with the rather small depressions produced by rubber. It seems preferable therefore to confine attention to camphor, where on account of the very large cryoscopic constant, the low molecular weight is apparently more certainly proved.

There is a two-fold experimental basis for the view that camphor and related solvents differ from benzene in hat they are capable of giving true molecular dispersions of rubber. (*a*) It has been stated [2] that rubber dissolves rapidly in camphor and menthol, without previous swelling, and gives mobile solutions. (*b*) Evidence has been presented [3] to show that, in distinction to the results of the osmotic and viscosity methods, the molecular weights found by the Rast method are independent both of the type of rubber used and of the concentration of the solution.

Two aspects of the Rast method call for comment : (1) the actual method of carrying out the experiments, and (2) the interpretation of the results obtained. The most obvious objection to the Rast procedure is that it involves heating together camphor and rubber at a temperature of about 180°. Our first experiments showed that in the presence of air rapid and extensive degradation occurred. After heating with camphor in a sealed tube for half an hour at 180° the viscosity molecular weight of crêpe (determined in benzene) had fallen to one-sixth, while on longer heating (1–2 hours) a brown oily material distilled on to the cooler parts of the tube. This degradation was completely prevented by evacuating the tube carefully before heating, and when this was done the rubber dissolved only after heating with camphor for several hours, giving first a swollen gel and finally a typical rubber solution of high viscosity (a 7 per cent solution of sol rubber in camphor at 180° was too viscous to flow). This simple observation alone disposes of the first part of the evidence in favour of a micellar structure for rubber. It also makes clear that if the freezing-points of rubber-camphor solutions are to be measured at all a vacuum technique is essential.

In its simplest form, the Rast method consists in determining the melting-point of camphor and of camphor plus rubber by the usual melting-point tube method employed in the identification of organic substances. This procedure does not readily lend itself to vacuum operation, even if its accuracy were sufficient for the present purpose. The technique of Reilly and Pyne [4] gives a more precise modification based on the determination of cooling curves for the solvent and solution. The design of an apparatus in which this can be done *in vacuo* is conditioned by the necessity of heating the whole of the evacuated portion in order to prevent rapid sublimation of camphor; the design finally adopted is shown in Fig. 32 (V[3]).

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[1] See Memmler, *The Science of Rubber*, pp. 232, 490.

[2] *Ibid.*, p. 232.

[3] Gee and Treloar, *I.R.I. Trans.*, 1940, *16*, 184.

[4] *Loc. cit.*

The thermometer (an Anschütz type graduated to 0·1°) was completely enclosed in the evacuated tube. It was suspended from a tungsten hook and centred in the solution compartment by a constriction in the body of the tube. The side-tubes *A* were provided so that the solution could be concentrated by distilling off camphor without opening the tube; the amount removed was determined by sealing off the side-tube into which the camphor had been distilled and weighing its contents. Four side-tubes were employed in the final series of measurements, rendering possible observations at 5 concentrations with a single filling. Rubber was introduced through *B* in the form of a benzene solution which was evaporated to dryness and finally evacuated thoroughly at 50°–60° before weighing in the camphor, re-evacuating, and sealing off *B*. The tube was completely immersed in liquid paraffin in a cylindrical Dewar vessel of internal diameter 5 cm. This bath was heated electrically by a wire wound as uniformly as possible on a glass tube fitting fairly closely into the Dewar and extending practically the full depth of the bath. A spacing of *ca.* 1 ml. between the turns of wire was sufficient to enable the important temperature range to be read accurately. The oil was efficiently stirred by a stream of nitrogen, and the heater current maintained constant by manual adjustment. In plotting a cooling curve the heater current was adjusted so as to make the rate of cooling of the melt 0·2° to 0·4°/min.: higher cooling-rates did not give sharp breaks in the cooling-curve, while lower rates were difficult to maintain constant. The thermometer was read every ¼ minute through a lens, mounted in a tube to reduce parallax errors.

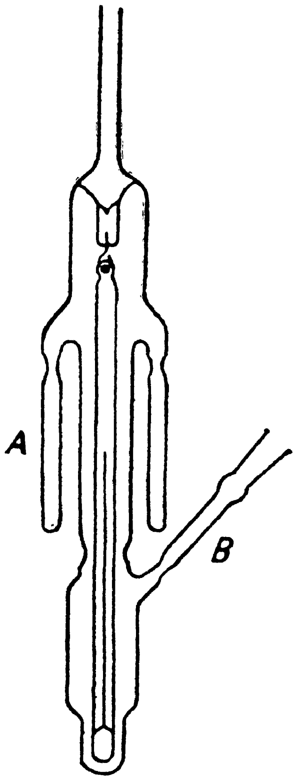

FIG. 32 (V[3])
Modified micro-freezing-point apparatus of Gee and Treloar

The camphor employed was a commercial specimen purified by resublimation *in vacuo* at 100°. Its freezing-point was repeatable on successive determinations to better than 0·1°; removal of about half of the camphor by distillation did not change the melting-point of the remainder significantly. With separate assemblies of the apparatus the melting-point of the camphor could be reproduced to about 0·1°. Difficulties were encountered when rubber solutions were employed; repeated attempts failed to give consistent results for solutions of crêpe, sol rubber or an intermediate fraction.[1] The trouble arose from the high viscosity of the solutions, which made it impossible to ensure that the solutions were homogeneous, and also retarded the attainment of thermal equilibrium. More successful results were obtained with a heavily milled crêpe, but the final experiments were carried out with a thermal degradation product prepared by Bolland. This material had a viscosity molecular weight of 53,000, and an osmotic molecular weight of 34,000, both measured in benzene plus 15 per cent MeOH. Camphor solutions containing up to 15 per cent rubber (by weight) were reasonably mobile and their cooling-curves showed sharp breaks: some typical results from Gee's paper[1] are given in Fig. 33 (V^3).

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[1] Bloomfield and Farmer, *I.R.I. Trans.*, 1940, *16*, 69.

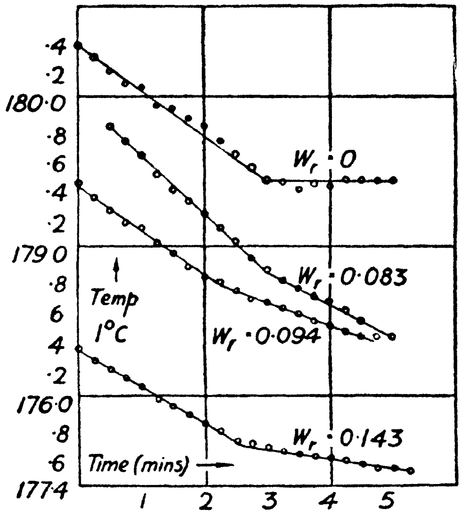

FIG. 33 (V^3)

Cooling curves from camphor-rubber mixtures

In this range of concentration the freezing-points were reproducible to *ca.* 0·1°, giving a probable error of 0·2° in the depression. At higher concentrations the error increased rapidly and the cooling-curve of a 19·8 per cent solution showed no detectable break: the figure given in Table I was estimated from the temperature at which crystallization spread through the solution surrounding the thermometer, and may easily be in error by 1°. The freezing-point depressions θ are given in the following table as a function of the weight fraction w_r of rubber for 2 separate series of measurements (w_r is calculated from the weights of rubber and camphor introduced, corrected for the weight of camphor vapour in the tube).

Series 1			Series 2		
w_r	θ	10^{-3} M′	w_r	θ	10^{-3} M′
0·105	$0{\cdot}7_5$	$6{\cdot}_2$	0·083	$0{\cdot}6_0$	$6{\cdot}_1$
0·198	$4{\cdot}_5$	$2{\cdot}_2$	0·094	$0{\cdot}7_4$	$5{\cdot}_6$
			0·106	$0{\cdot}7_4$	$6{\cdot}_4$
			0·143	1·8	3·7
			0·161	3·2	2·4

The apparent molecular weights M′ were calculated from the equation

$$10^{-3}\mathrm{M}' = \frac{40}{\theta} \cdot \frac{w_r}{1 - w_r} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

They are several times larger than those previously reported and are clearly not independent of the concentration, even allowing for the large experimental error at the lower concentrations. Similar results were obtained in measurements made with milled crêpe solutions. Fig. 34 (V^3) records the apparent molecular weights of rubber in various solvents.

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[1] *Loc. cit.*

Niederl's Vaporimetric Micro-molecular Weight Method. In this method, the substance, solid or liquid, is placed in a suitably shaped glass vessel which is otherwise filled with mercury. The apparatus is heated in a bath to a known temperature which vaporizes the substance and causes an equal volume of mercury to be expelled: this mercury is collected and weighed. The volume of a known weight of vapour having been found in this way, the weight of 22·4 litres at N.T.P. can be calculated. Two forms of apparatus are used according as the substance vaporizes at a low or a high temperature.

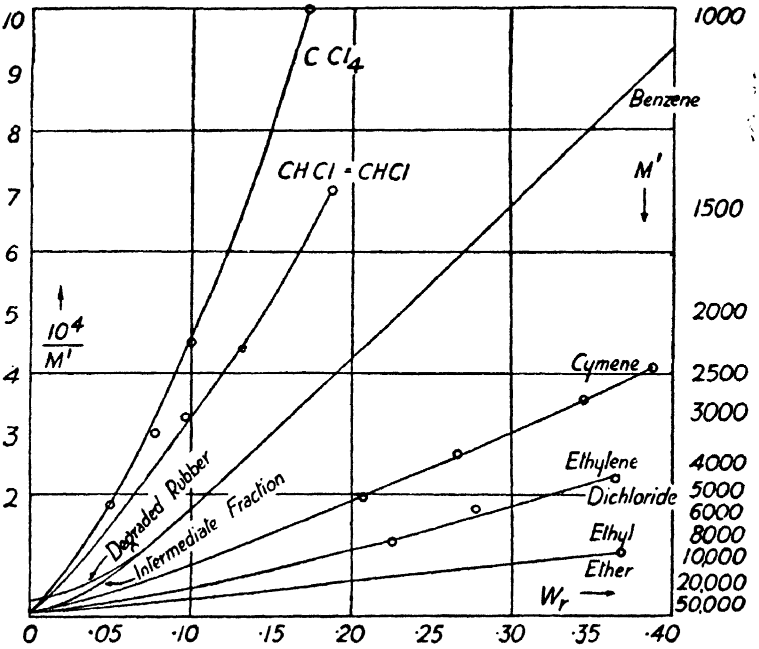

FIG. 34 (V^3)
Molecular weight of rubber in various solvents

Low Boiling-point Apparatus.[1] A diagram[2] of this is shown in Fig. 35 (V^3), where *A* is a bulb of 100 ml. with a vertical tube *B* about 10 cm. long and just wide enough to take a thermometer shown at *C*. The side-arm *F* has a bore of 3 mm., the horizontal part is 6 cm. long and the vertical part long enough to reach about 2 cm. above the edge of the boiling-vessel; it fits into the vaporizer by means of the ground-glass joint *E*. Thermal contact between the bulb of the thermometer *C* and the wall of the jacket is ensured by a little mercury at *D*. The vessel in which the expelled mercury is collected is shown at *H*. The liquid in *G* is water so that this form of apparatus is suitable for liquids boiling below 100°. Before use the vaporizer is washed out three times by shaking with 2 ml. of acetone; it is then heated in an oven at 100° and is evacuated by connexion to the pump while it is still hot.

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[1] *Z. analyst. Chem.*, **1929**, *77*, 169; *Ind. Eng. Chem., Anal.*, **1935**, *7*, 214.

[2] *Ibid.*

Filling. Weighing-pipettes are prepared from 6 mm. soft glass tubing by softening the glass in the non-luminous flame, removing it and while rotating it on its axis drawing it out into a 2-mm. bore capillary which is then cut into 10-cm. lengths. One of these is heated at the middle in the flame of the micro-burner until the walls collapse, when it is pulled out into a solid thread 3 cm. long by 0·5 mm. diameter, rotating all the time. The thread is heated at the centre and divided into two and a small round knob formed at the end. The open end is now drawn out so as to leave a bulb 3 to 5 mm. long with a fine capillary stem, 0·1 mm. in diameter and 10 to 15 mm. in length. The pipettes are kept in a desiccator. After weighing the empty pipette, a little of the liquid is placed on a watch-glass, the open end of the capillary is put under its surface and the bulb is warmed gently with the flame of the micro-burner ; on cooling, a partial vacuum is created and some of the liquid is forced into the bulb ; this is centrifuged to the end of the bulb away from the capillary which is then sealed. After cooling, the outside is wiped and treated in just the same way as the empty pipette was, and is weighed.

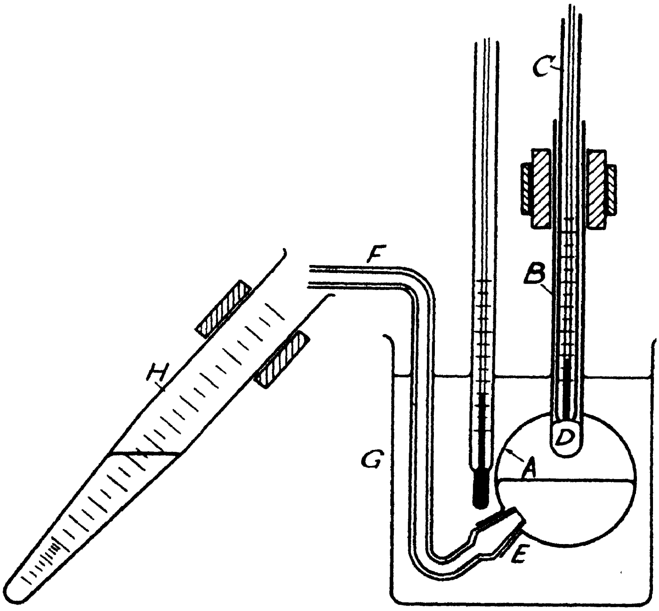

FIG. 35 (V*)
Micro-molecular-weight apparatus (vaporization method)

The mercury is purified by shaking with conc. sulphuric acid and then pouring in a fine stream through 1 in 10 nitric acid. Next it is washed in a separating funnel with water, acetone and distilled water. Finally, after removing the water it is heated in a round-bottomed flask to 250° on a sand-bath : a two-holed stopper carries a glass tube ending in a very fine capillary below the mercury surface and also a glass tube connected to the water pump so that a partial vacuum is maintained while a small air current passes through ; this treatment is to make sure of the absence of all volatile impurities.

The pipette is now cut about 1 mm. along the capillary from the bulb, and both pieces are put in the vaporizer. Mercury is added, tilting the vessel so that it is filled to the top of the ground-glass joint. The joint on the side-arm is very slightly greased and is pushed home and some mercury is pushed into the side-arm which is then filled by means of a tube drawn out fine at one end so that it will go into the tube and with a rubber bulb attached to the other end. Mercury is forced out of the tube by pressure on the bulb and air bubbles are removed by putting a wire down *f* and moving it about ; this procedure is continued until the whole of *f* is filled. The mercury is put in *d* and the thermometer inserted and the vaporizer placed in the water in *g*, where it is left until it and its contents are at the same temperature as the water, as is shown by the two thermometers giving the same reading. After seeing that the mercury is right up to the end of the tube *f*, the vaporizer is placed in the position shown in the diagram with the collecting-tube under the open end of *f*. The water in *g* is boiled until both thermometers show the same temperature, when the experiment is stopped and the mercury which has been expelled is weighed.

A correction is necessary for the expansion of the glass and the mercury. This is obtained by carrying out an experiment in which the capillary used is an empty one ; if in this the amount of the mercury expelled is expressed as $c(T_2 - T_1)$ when the apparatus is heated from the temperature T_1 to T_2, we can get the value of c, the amount of mercury expelled for a rise of one degree.

The molecular weight can now be calculated by substituting in the expression

$$M = 62351\,\frac{\text{wt. } s(273 + T_2)}{VP}$$

$$V = \frac{g - c_1(T_2 - T_1)}{d} - vs$$

$$P = p_1 + p_2 - p_3 + p$$

where wt. s = weight of the sample
V = volume of the vapour
g = weight of mercury expelled
c_1 = the constant as determined above to allow for expansion of mercury &c.
T_1 = initial temperature
T_2 = final temperature
d = density of mercury at $T_2°$.
vs = volume of sample = (m/density), approx. 1 cu. mm. per mg.
P = pressure of vapour
p_1 = barometer reading
p_2 = vertical distance in mm. from outlet of *f* to mercury surface in *a*

wt. p_3 = vapour pressure of mercury at T_2

p = capillary depression in mercury at open end of f (+ 8 mm.); temperature reduction of barometer (− 2 mm. at 15°, − 4 mm. at 32°); density reduction of mercury in f which is in hot liquid (− 1 mm. if $T_2 = 320°$). The net value is so small that it can generally be neglected with respect to P.

Optical Method. An optical method for molecular weight determination has been developed by P. Debye [1] which depends on the fact that the amount of light scattered by a solvent is increased by the introduction of a solvent is increased by the introduction of a solute in small concentration.

An analogy exists between this method and the Osmotic Pressure method in that the turbidity of a solution is proportional to the concentration of solute particles.

The turbidity (τ) of a solution is given by the formula

$$\tau = \frac{32\pi^3}{3} \cdot \frac{\omega_0^2 (\mu - \mu_0)^2}{\lambda^4} \cdot \frac{1}{n} \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where μ_0 = Refractive index of the solvent

μ = refractive index of the solution

both for light of wave-length = λ

n = number of solute particles per ml., of solvent.

For practical purposes n is expressed in terms of the concentration c (in grams per ml.), the molecular weight M, and Avogadro's number N, so that equation (i) becomes

$$\frac{\tau}{c} = \frac{32\pi^3}{3} \cdot \frac{\mu_0^2}{N\lambda^4} \cdot \left(\frac{\mu - \mu_0}{C}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

Corresponding equations have been deduced [2] for (*a*) smaller particles in more concentrated solutions, and (*b*) larger particles at higher dilutions.

The experimental arrangement in the application of Debye's turbidity method to this determination of molecular weights involves two measurements: (1) A measurement of the difference between the index of refraction of the solution μ and that of the solvent μ_0, and (2) The turbidity.

With reference to (1), one single measurement at a given concentration c, say of 1 per cent, is usually sufficient, since the difference $\mu - \mu_0$ is generally very accurately proportional to c. Usually this difference is of the order 0·001 for a 1 per cent solution. The fifth decimal must be known in order to ensure an accuracy of the order of 1 per cent of the quotient $(\mu - \mu_0)/c$. Debye uses a differential refractometer, consisting of a hollow large-angle prism (140° angle) which contains the solution and which is immersed in a rectangular cell containing the solvent. The cell is interposed between two lenses (focal length 70 cm.). In the focal plane of the first lens is a slit illuminated with the same monochromatic light as that used for the monochromatic light as that used for the scattering measurements. In the focal plane of the second lens the image of the slit is observed in an eyepiece equipped with a filar micrometer. As a monochromatic light source a mercury arc, AH-4 with the appropriate light filter is used. The instrument is calibrated with sucrose solutions and water. The displacement of the slit image is proportional to $\mu - \mu_0$ and a difference of 0·001 corresponds to a displacement of 3 mm., which is amply sufficient to ensure the required accuracy.

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[1] *J. Phys. Chem.*, 1947, *51*, 18.

[2] *Loc. cit.*

With regard to the turbidity, the instrument used for this purpose is so contracted that a slightly convergent beam of monochromatic light, again furnished by a mercury arc, and the appropriate filter is focused in the interior of a test tube containing the liquid, entering through the bottom of the tube. The light scattering in directions near 90° with respect to the direction of the primary beam falls on a photocell. The resulting photocurrent is amplified in a D.C. amplifier and read on a microammeter. Another photocell receives a small part of the primary light and serves as a check on the constancy of the light source. With current regulation of the mercury arc by means of a special ballast lamp circuit,[1] this particular arrangement gives stable, reproducible meter readings. The excess scattering of the solution as compared with the solvent is measured as the difference in reading of the microammeter for the test tube filled with solution and filled with solvent. For the most sensitive setting of the amplifier, one scale division of the microammeter corresponds to a turbidity of 5×10^{-6}cm.$^{-1}$, a result which means practically that reliable measurements can be made with solutions which scatter as little as 20 per cent more than the pure solvent.

The absolute value of the turbidity is determined with the help of a standard, a solution of polystyrene in toluene of known turbidity in a sealed test tube. For details of methods, including improved designs by Debye, see references.[2]

[1] General Electric Model B–47.

[2] *J. Appl. Physics*, 1946, *17*, 392.

CHAPTER VI[3]

DIFFUSION

SECTION 1: MEASUREMENTS

FICK'S Law. The first diffusion law of Fick states that the quantity *ds* of dissolved substance passing in time *dt* across a thin section of area A in which the concentration gradient is $\frac{dc}{dx}$, is given by

$$\frac{ds}{dt} = \mathrm{DA}\frac{dc}{dx}$$

where D is the diffusion coefficient.

The change of concentration with time is given by the second law

$$\frac{dc}{dt} = \mathrm{A}\frac{d^2c}{dx^2}$$

The solution of this differential equation has been worked out by Stefan[1] for cases in which the diffusing solution is overlaid by a very tall column of pure solvent. The original paper gives tables of the quotient $\frac{h}{2\sqrt{\mathrm{D}t}}$ for values from 0·10 to 0·60, where h is the height of each of the sixteen layers in which the water column is divided, and t the time of diffusion in days. The original weight of dissolved substance is taken as 10,000. From these tables, and a knowledge of the composition of the sixteen layers above the solution, the diffusion coefficient D can readily be found.

From the purely physical point of view diffusion is a very wide term, covering the diffusion of gases in gases, liquids, and solids, of dissolved solids in liquids and of solids in solids. In addition, the movement of the atoms or molecules of a substance among each other—so-called self-diffusion—has revealed a very interesting and theoretically important field of work in recent years. The physical chemist, however, is chiefly concerned with diffusion of solids in liquids, and of gases and solids in solids, and it is only with these topics that this section deals.

Diffusion in Liquids. The outstanding difficulty in measuring diffusion in liquids is the influence of convection currents. Hence the most rigorous precautions must be taken to ensure absolute uniformity of temperature in the diffusion cell and its surroundings. Descriptions of older forms of apparatus, and of the precautions necessary in their use, are given by Arndt.[2] In more recent years attention has been focused on diffusion of colloids as a means taken in conjunction with sedimentation data, of determining molecular weights, and special forms of apparatus have been devised for the purpose. Thus Tiselius Gross[1] measured diffusion at a boundary in a tube at rest by the method of light absorption. The absorption is determined photographically, but possible irregularities in the sensitivity of the emulsion, and traces of impurities in the diffusing solutions, create difficulties.

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[1] *Sitzungsber. d. Wien. Akad.*, 1879, *79*, 161.

[2] *Physikalisch Chemische Technik* (Enke, 1923).

These difficulties are avoided in the refractometric method originally developed by Lamm and Polson for use in the ultracentrifuge, and later[2] combined with the Svedberg diffusion cell as a static diffusion apparatus (Fig. 1 (VI^{3})).

The protein solution was placed in the limb *d* and the buffer or solvent in limb *a*, which had an inner diameter of 1 cm. The tube was placed in a thermostat controlled to within 0·005° and when thermal equilibrium had been reached the stopcock *c* was opened and the protein was forced through the capillary tube *b* by slowly increasing the air pressure on the solution in limb *d*. When the boundary between the two solutions had reached a suitable position in limb *a* the stopcock was closed.

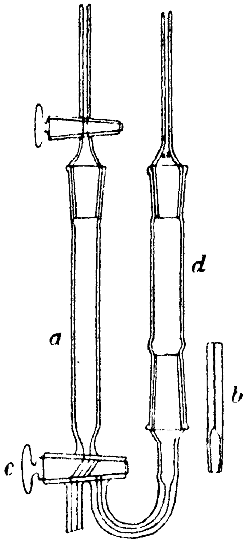

FIG. 1 (VI^{3})
A static diffusion apparatus

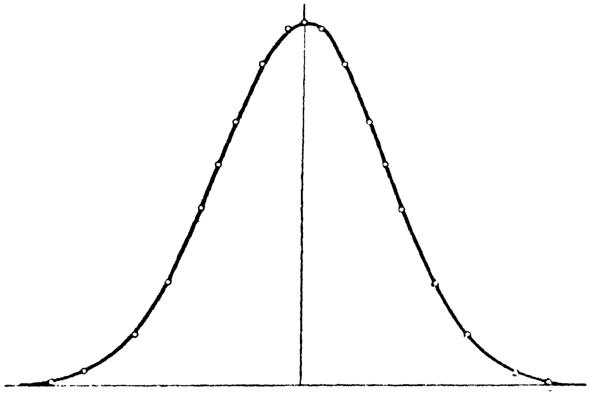

FIG. 2 (VI^{3})
Diffusion gradient curve for ovalbumin

The principle of the refractometric method depends on photographing a uniform transparent scale through the diffusion cell. The refractive index gradient at the boundary produces a distorted image of the scale in which scale line displacement is proportional to the concentration gradient when the refractive index is a linear function of the concentration. The light used is provided by a quartz mercury arc lamp, fitted with a filter which transmits light of a wave-length not absorbed by the solution examined. Fig. 2 (VI^{3}) shows a diffusion gradient curve for ovalbumin. The circles represent the ideal distribution. The abscissa axis is the direction of the diffusion process.

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[1] *Kolloid-Z.*, 1934, *66*, 12.

[2] *Biochem. J.*, 1936, *30*, 528.

The mathematical treatment of the results is rather complicated, and reference should be made to the original paper.

Other types of diffusion cell, some of them requiring not more than 2 ml. of solution, have been designed by Stamm and Loughborough,[1] by Furth and Ullmann,[2] and other workers. The Furth cell is particularly ingenious ; it is built on a microscope slide and the dye solution being studied is brought into contact with the pure solvent by removing the metal bar separating them by an electromagnetic arrangement. A solution of the dye in an adjacent compartment serves as a colorimetric standard, and diffusion is followed with a movable microscope.

Diffusion in Electrolytes. A rapid method for the study of diffusion of substances in solution was originally devised by Northrop and Anson in 1928.[3] It consists in separating two homogeneous bodies of a solution by an indifferent membrane with pores of visible or microscopic size, confining the diffusion gradient to within this membrane. The method has been improved and standardized by McBain and Liu.[4] They used cells obtained from the Jena Glasswerke.[5] They found it advantageous to have the sintered glass directly fused to the remainder of the cell. The following details of the experimental technique are from the original paper of McBain and Liu.[6] The pore diameter of the sintered glass designated as G-4 was found to be most suitable for the diffusion experiments and the cells required no alteration before use except to grind away the slightly projecting edge of the glass. The cell is shown in Fig. 3 (VI³), dipping into a closely fitting beaker of water. They have found that the procedure given in the following paragraph enabled them to obtain the results already indicated without any elaborate precautions for the avoidance of vibration or extreme constancy of temperature. The results are necessarily relative but are standardized, as in using a conductivity cell, by a measurement of a single standard solution such as 0·1 N potassium chloride, of which the absolute value is already established.

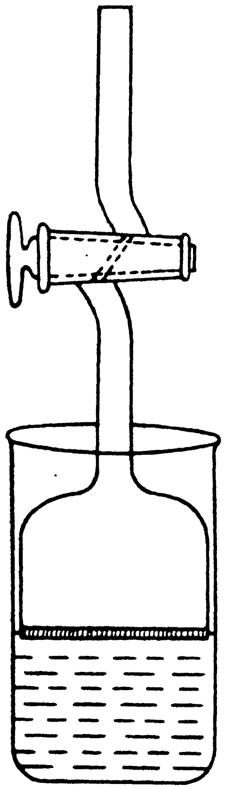

FIG. 3 (VI³)
Diffusion cell

After testing for leaks, the volume of the diffusion cell up to the glass stop-cock is determined by weighing. It is then suspended by a 5-mm. rubber tube about 15 cm. long and the suspension or stem adjusted until the diaphragm is accurately horizontal as tested against a large mercury surface. This is to minimize the possibility of streaming through the diaphragm. The cell is first cleaned by sucking cleaning solution through the porous disk, using a water pump at the upper end. The liquid is expelled again by applying a pressure of not more than 1 metre of water. After thorough rinsing, water, freed from dissolved gas by boiling or shaking *in vacuo*, is drawn through the diaphragm in order to dissolve any air therein. Bubbles are dislodged by sudden increase in suction, which may serve as a test for the removal of air. In removing the water the pressure is released just as the last layer is about to enter the diaphragm.

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[1] *J. Phys. Chem.*, 1936, *40*, 1113.

[2] *Kolloid-Z.*, 1927, *41*, 300.

[3] *J. Gen. Physiol.*, 1929, *12*, 543.

[4] *J. Amer. Chem. Soc.*, 1931, *53*, 59.

[5] Made by Schott & Genossen, Jena, Germany.

[6] *Loc. cit.*, pp. 60–1.

The solution to be investigated is freed from dissolved gas by boiling for a few minutes at room temperature in the vacuum of a good water pump. The cell is then rinsed and charged with the solution through the diaphragm and filled completely without bubbles, past the stop-cock which is then closed. The cell is first immersed in a large beaker of pure, gas-free water, and before placing it in the surface of the beaker of gas-free water as shown the last drop of adherent water is removed by slightly tilting the diaphragm and touching it with a glass rod.

The preliminary diffusion proceeds for a few hours or whatever time is necessary to establish a steady diffusion column within the disk. This can be calculated from the time required for that part of the solution which is within the diaphragm to diffuse out entirely; for hydrochloric acid about 2 hours is required. Finally, the cell is transferred, after removal of adherent liquid as before, to a clean beaker containing a quantity of gas-free water equal to the volume of the cell. The space between the cell and beaker is closed with a ring of rubber dam to minimize evaporation. The measurement now begins. The preliminary diffusion not only creates the uniform diffusion gradient within the diaphragm but enables the solutions to attain the temperature of the thermostat in which the apparatus is placed.

After sufficient diffusion has occurred to permit of an accurate analysis of the dilute solution formed in the beaker, the cell is removed and wiped with filter paper, including the inside of the tubing above the stop-cock. The solution is extruded through the diaphragm, the first 10 ml. or so being discarded and a sample of the remainder being taken for analysis.

They made use of cells whose diaphragms had the following characteristics.[1]

Material	Trade designation	Approximate pore radius, Å	Diameter and thickness, cm.
Glass	G-3	$(15–20) \times 10^4$	$5 \times 0{\cdot}2$
Glass	G-4	$(2–5) \times 10^4$	$5 \times 0{\cdot}2$
Alundum[2] . . .	RA225	$(8–10) \times 10^4$	$5 \times 0{\cdot}2$
Alundum. . . .	RA98	$(10–15) \times 10^4$	$5 \times 0{\cdot}2$

The glass diaphragms allow faster diffusion than those of alundum. Diffusion in the finer glass diaphragm is as fast as in the coarser one, while the possibility of streaming is eliminated. It will be noted that the pores have about 10,000 times the diameter of such large molecules as sucrose and one or two thousand times the diameter of haemoglobin or the smaller particles of blue gold.

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[1] The pressure required to force air bubbles freely through the diaphragms under water confirmed the radii ascribed to the alundum disks but indicated slightly smaller values than those here given for the glass diaphragms.

[2] Norton Co., Worcester, Massachusetts.

According to McBain, Dawson, and Barker,[1] diffusion through porous membranes (using a similar type of apparatus as above) of constant properties is one of the simplest, quickest, and most accurate methods of determining particle size or molecular weight of molecules larger than sucrose that are approximately spherical. Only at the isoelectric point or, with less certainty, in the presence of buffers is the true molecular weight obtained. For egg albumin 34,000 was found. At other values of *p*H or with insufficient or unsuitable buffering widely divergent values result from the phenomena of the mutual acceleration and retardation of ions and charged particles. Thus charged colloids may be found to diffuse faster than ordinary molecules.

Diffusion Velocity of Glucose. It has been shown by Friedman and Carpenter [2] that the molecular weight of simple non-electrolytes can be calculated from diffusion coefficients determined at infinite dilution: (1) by an examination of the values of the diffusion coefficient to be found in the International Critical Tables; and (2) by experimental study of the diffusion velocity of glucose.[3] An apparatus similar to that employed by McBain and his co-workers was employed and their procedure was also followed. Because of the extremely low concentrations resulting in the outside solution, this method effectively measures diffusion against water. Cell constants were calculated from the diffusion coefficient of potassium chloride as listed in the 'International Critical Tables' from the work of Öholm. The glucose concentrations were measured by determining the amount of potassium iodate needed for complete oxidation of a sample.[4]

All experiments on glucose were carried out at 25° and several determinations of diffusion velocities were made at each concentration. The results of this study are given in the table, in the third column of which the apparent molecular weight of glucose has been calculated from the diffusion coefficient obtained at each concentration.

DIFFUSION OF GLUCOSE AT 25°

Concn.	D in cm.^{2}/day	Calcd. mol. wt.
0·60	0·535	237
0·50	0·539	232
0·40	0·543	227
0·355	0·546	223
0·30	0·550	218
0·25	0·552	216
0·20	0·556	211
0·10	0·566	200
0·00 (extrap.)	0·586	180

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[1] *J. Amer. Chem. Soc.*, 1934, *56*, 1027.

[2] *Ibid.*, 1939, *61*, 1745.

[3] *Loc. cit.*

[4] Williams, Rohrman, and Christensen, *J. Amer. Chem. Soc.*, 1937, *59*, 291.

The experimental values are given graphically in Figs. 4 (VI³) and 4*a* (VI³), in which it is evident that when sufficiently accurate diffusion data are obtained, it is possible by plotting diffusion coefficient against square root of the concentration to extrapolate to infinite dilution and thus obtain the value of diffusion coefficient that will yield the correct molecular weight when substituted in the Stokes-Einstein diffusion equation.

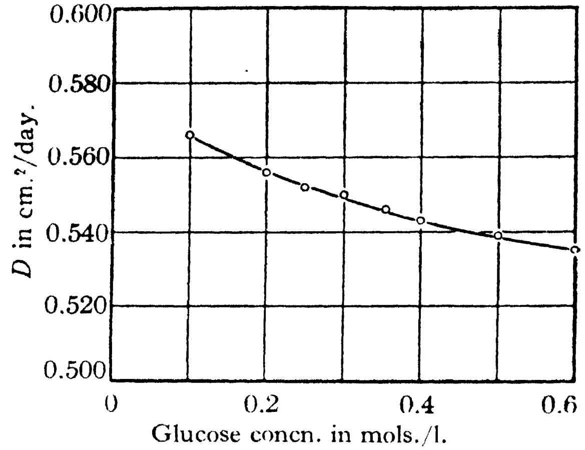

FIG. 4 (VI³)
Diffusion of glucose at 25°. Diffusion coefficient plotted against sugar concentration

An instrument known as a microdiffusionmeter has been constructed by Furth [1] for the measurement of the diffusion in coloured and uncoloured liquids. One of the methods for this measurement is based on the observation of the index of refraction of the liquid which is a unique function of the concentration. The diffusion chamber is cemented to one of the side-faces B of a rectangular prism PR (Fig. 5 (VI³)). Monochromatic parallel light

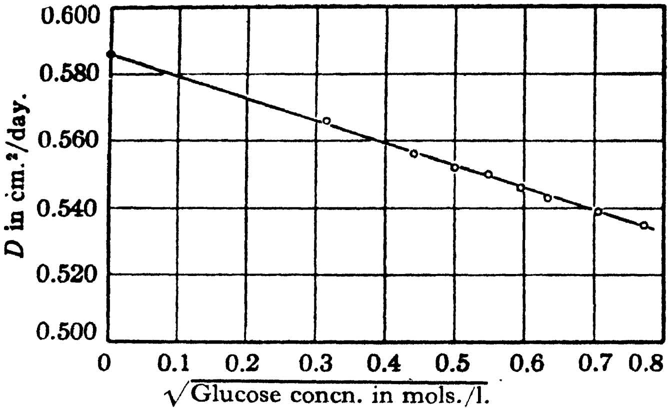

FIG. 4*a* (VI³)
Diffusion of glucose at 25°. Diffusion coefficient plotted against square root of sugar concentration

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[1] *J. Scient. Inst.*, 1945, *22*, 61.

falls on the hypotenuse face C of the prism and is refracted into the diffusion chamber. Observation is made through a microscope directed normally against the ground-glass wall E of the diffusion chamber. The chamber is first filled with a solution of uniform concentration *c*. The field of observation will then in general show two regions, a dark and a light one separated by a vertical boundary. The prism is now slowly rotated anti-clockwise about a vertical axis across the field of observation until it reaches the right-hand edge (as seen in the reversed image provided by the microscope). The field then becomes completely dark because total reflexion at the wall B of the diffusion chamber sets in. In this position the prism is fixed. The chamber is now prepared for the diffusion experiment proper and the diffusion started by pulling out the slider. The concentration within the chamber will now vary with height and the boundary between the dark and light regions is no longer a straight line but a curve. The intersection point (S) of this curve with the right-hand edge obviously marks the level at which the concentration in the chamber has the value *c* at the time *t* of observation. By measuring the distance *x* of S below the slider level *o* (again keeping in mind that the image is reversed) at different times the propagation of this concentration and the corresponding *x*–*t* line can be drawn. By repeating the experiment for different concentrations, i.e. for different angular positions of the prism, the material for the measurement of the propagation of different concentrations is obtained, and the determination of D as a function of *c* then proceeds in exactly the same manner as for coloured solutions.

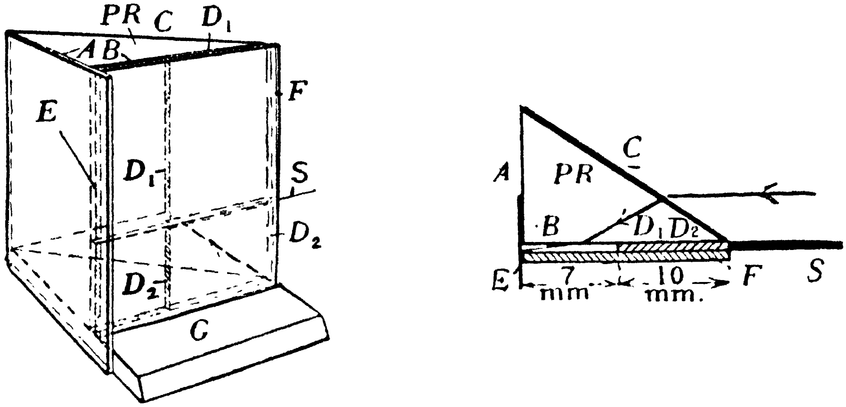

FIG. 5 (VI^3)
Diffusion chamber for the measurement of colourless liquids

Diffusion of Solids in Solids. This type of diffusion was first observed by Roberts-Austen,[1] and the earliest measurements on the diffusion of gold in solid lead are due to him. The method was simply to weld a thin disk of gold on to a lead bar, which was then kept at a high temperature for many days. At the end of the diffusion period the bar was cut up into a number of sections, and the gold content of each determined. From the

[1] *Proc. Roy. Soc.*, 1900, *A 67*, 101.

results, and Stefan's tables, the diffusion constant of gold in lead was calculated; it was found to be 5 × 10^{-3} cm.^{2} per day at 165°.

Later work by von Hevesy, Seith,[1] and others showed that this figure was an abnormally high one. When the diffusing gold was replaced by silver, cadmium, mercury, bismuth, and thallium progressively decreasing rates of diffusion were observed, that of tin in lead being only about three times greater than of lead in lead at 250°. It was suggested that as the similarity between the two metals increased the coefficient of diffusion of one in the other fell off.

On this theory the self-diffusion of the atoms of a metal should be very slight. Such self-diffusion can be studied by using natural or artificial radioactive isotopes, and the results of experiments have fully confirmed expectations.

A typical example is the 'self-diffusion' of gold as studied by McKay.[2] Because of the very low rate of diffusion a thin gold sheet (0·1 mm.) had to be taken. This was shielded by gold on one side and by cadmium on all sides, and was placed along with a radium-beryllium source of neutrons near the centre of a block of paraffin wax. Neutrons within a certain velocity range could pass through the cadmium but were very strongly absorbed by the gold, and the result of this treatment was to produce a gold disk with a much greater activity on one side than the other. The actual activities were measured by a Geiger-Müller counter.

On keeping the disk at a high temperature (700°–1,000°) for a considerable period the radioactive atoms diffused through the disk, and hence the activities on the two sides tended to become more nearly equal. To allow for radioactive decay a second gold disk was given an exactly similar treatment to that under test, but was kept at ordinary temperatures so that diffusion was negligible. From the counts on the two sides of the heated disk at different times, corrected for the decay loss, the self-diffusion constant of gold could be calculated; it was found to be

$$0{\cdot}38 \times 10^{-5} \text{ mm.}^2/\text{min. at } 819^\circ$$

Diffusion of Gases in Solids. The earliest observations of the diffusion of gases in solids are due to Cailletet, who found that on immersing an iron vessel in dilute sulphuric acid some of the hydrogen evolved passed through the metal and appeared inside the vessel. Later investigation [3] confirmed the earlier belief that at ordinary temperatures this phenomenon was exhibited only by nascent hydrogen, formed by reduction or at the cathode; diffusion of molecular hydrogen could not be detected till the temperature was raised to 350°.

Reaction between Gases and Metals. (See Vol. II, p. 24.) The subject of gaseous diffusion into solids is of great importance in metallurgical research in the study of catalysis and in the production of highly evacuated apparatus. Fortunately a study on this topic has been made by Smithells [4] and his text must be consulted for a detailed account of the whole problem embracing adsorption, diffusion, and solution of gases in metals. All that will be attempted in this section is to outline the direct method of determining the solubility of a gas in a metal. The principle of the method consists in bringing a weighed amount of metal in a calibrated vessel into contact with the gas at a known pressure and temperature, and when equilibrium is reached the change in pressure and temperature of the gas is noted. The pioneer work of Graham, and since then of a large number of other workers, has shown that a small number of metals are permeable to hydrogen and also oxygen and nitrogen in the molecular state. The diffusion is slight at ordinary temperatures, but increases rapidly as the temperature is raised. Several equations have been proposed to explain the experimental results. The most generally successful, and one which has also a theoretical foundation, is Richardson's

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[1] e.g., *Z. Electrochem.*, 1931, *37*, 528; *ibid.*, 1933, *39*, 33.

[2] *Trans. Faraday Soc.*, 1938, 845.

[3] *Cf.* Charpy and Bonnerot, *Compt. Rend.*, 1912, *154*, 592.

[4] *Gases and Metals. An Introduction to the study of Gases*, Chapman & Hall, London, 1937.

$$\mathrm{D} = \mathrm{K}\frac{1}{d}p^{\frac{1}{2}}.\mathrm{T}^{\frac{1}{2}}.e^{-\frac{q}{T}}$$

where D is the rate of diffusion and d, p and T are respectively the density, pressure and absolute temperature of the gas. K is the diffusion constant.

Apparatus. Many different forms of diffusion apparatus have been designed by different workers to meet the particular requirements of various gas-solid systems, from the simple jacketed bulb used by Barrer [1] to measure diffusion through silica glass to the elaborate apparatus of Smithells and Ransley for diffusion in metals at high temperatures.

Borelius and Lindblom [2] studied the diffusion of nascent hydrogen in iron and nickel by using as cathode a metal tube of about 1·25 cm. diameter and having an initial wall thickness of 1·5 mm. This was turned down for about 10 cm. of its length, the lower end closed and the upper end connected to a manometer. After preliminary evacuation the tube was immersed in the electrolyte (2 per cent caustic soda solution). The rate of diffusion was calculated from the rise in pressure inside the tube, and the effects of current density, applied voltage, and internal gas pressure could readily be studied. Experiments at higher temperatures were carried out by immersing the cell in a suitable thermostat. Perhaps the most striking result of this and other similar work is that the rate of diffusion is independent of the pressure of gas inside the tube.

For work on the diffusion of molecular gases Smithells and Ransley [3] have designed apparatus (Fig. 6 (VI³)) in which the defects of earlier forms (variations in temperature, difficulties of securing absolute vacuum-tightness) are claimed to have been eliminated. *a* shows the diffusion bulb and *b* the exploring thermocouple. The method was to admit gas on the outside of a metal tube, which was sealed at one end and continuously evacuated on the other. The tubes, which were heated by passage of an electric current, with special precautions to eliminate cooling at the ends, were of diameter 2 mm., wall thickness 0·1 mm., and length 40–110 mm.

Temperatures were measured by a chromel-alumel thermocouple in a very fine silica sheath, which was clamped to an iron block moved to and fro by a magnet, so that the temperature at any part of the tube could be measured. The maximum variation in the temperature of the tube between the electrical leads did not exceed 10° at temperatures ranging

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[1] *J. Chem. Soc.*, 1934, 378.

[2] *Ann. Physik.*, 1927, *82*, 201.

[3] *Proc. Roy. Soc.*, 1935, *A 150*, 172.

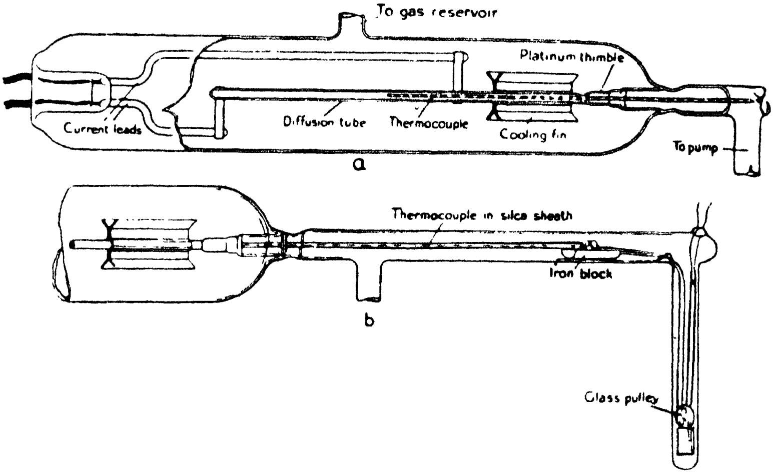

FIG. 6 (VI³)

(*a*) Diffusion bulb. (*b*) Thermocouple

up to 1,600°. Diffusion through that part of the tube outside the leads was prevented by clamping on a nickel cooling-fin.

The complete apparatus, which was baked out as far as possible before use, is shown in Fig. 7 (VI³).

The complete pump table consisted of two sections. The diffusion

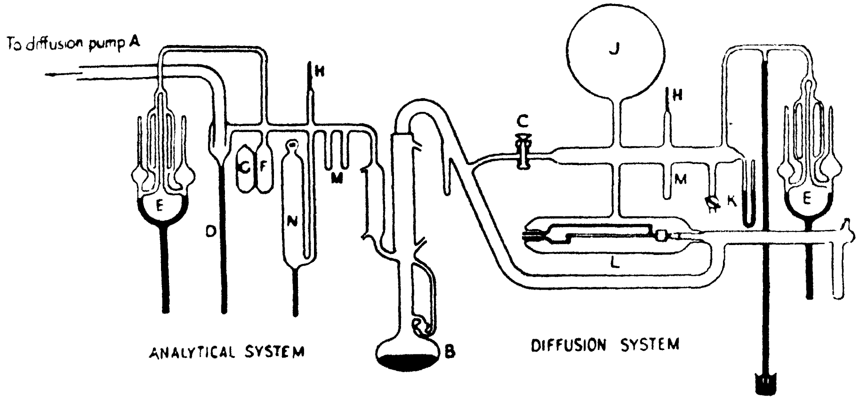

FIG. 7 (VI³)

General arrangement of diffusion apparatus

B, diffusion pump; D, mercury cut-off; EE, McLeod gauges; F, Pirani gauge; G, compensator; HH, palladium tubes; J, reservoir; K, to gas reservoirs; L, diffusion bulb; MM, freezing-tubes; N, compression bulb.

system was provided with two McLeod gauges and two manometers, covering a range of pressure from 760 to 10^{-6} mm. Hg. A palladium tube was added for the admission or extraction of hydrogen. The pressure during diffusion was maintained sensibly constant by having a large capacity bulb (3 litres) on the system. Traces of water vapour and condensible gases could be frozen out by applying a suitable freezing agent to the side-tube. A permanent connexion was made to glass reservoirs of gases other than hydrogen. The whole system could be evacuated to a pressure of about 10^{-6} mm. Hg by opening tap C.

A high vacuum was maintained on the inside of the diffusion tube by means of pump B, and the gas diffusing collected in the analytical system between the mercury cut-off D and this pump. The pressure was usually measured by means of the McLeod gauges, but a Pirani gauge was also incorporated and calibrated for the various gases used, and served as a useful check on the nature of the gas sample. This system enabled any gas that had diffused to be analysed by the usual methods of gas analysis at low pressures. This was found particularly useful in experiments with the rare gases, for the small amounts of gas collected in the analytical system were invariably found to consist of hydrogen, either present in the rare gas or evolved from some part of the apparatus.

The solubility of hydrogen in palladium has been investigated by Owen [1] using an X-ray method at pressures less than one atmosphere and at temperatures between 60° and 130°. There is no evidence of hydride formation and the results indicate two solid solutions. With rise in temperature there is an increase in the width and area of the hysteresis loops. The influence of pressure was also investigated.

Diffusion of Oxygen in Silver. Much of the earlier work has been carried out in hydrogen-platinum and hydrogen-palladium systems. These systems, however, cannot be regarded as typical and the systems oxygen-silver and hydrogen-silver have been selected by Steacie and Johnson [2] as more suitable for purposes of investigation. It will be described in some detail and is typical of a good type of apparatus. The following is an account of their method of obtaining the solution of oxygen gas in silver.

The principle is simple. A definite volume of gas was introduced into a bulb of known volume, which contained specially prepared silver foil, and was connected to a manometer. At any temperature the pressure of the gas in the bulb could be calculated from the gas laws. If any absorption took place, the observed pressure would be less than that calculated, and the difference between the two pressures would be a measure of the absorption. The apparatus from Steacie and Johnson's paper [3] is shown in Fig. 8 (VI[3]). Three bulbs, A, B, D, were contained in an electric furnace F. The bulb A was filled with air and led to a thermal regulator. D was part of a constant-volume gas thermometer. The third bulb B contained silver foil. The bulbs and connecting-tubes were made of either Pyrex glass or of quartz, and were connected to the remainder of the apparatus by means of de Khotinsky cement. The bulb containing the silver was connected, through the tap E, with a manometer IJ. A glass pointer M was sealed into the top of the tube J. By means of the taps H and K either the silver bulb or the gas thermometer could be connected to the manometer. The volumes of the tube J from the pointer M to the tap E, of the capillary tube from the tap to the furnace, and of the bulb containing the silver were all known. The furnace could maintain a temperature of 1,000°.

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[1] *Phil. Mag.*, 1944, *35*, 50; see also Owen and Williams, *Proc. Phys. Soc. London*, 1944, *56*, 52.

[2] *Proc. Roy. Soc.*, 1927, *117*, 662; 1926, *112*, 542.

[3] *Loc. cit.*

The tube J was connected to one arm of a two-way tap O. The other arm of the tap led through a phosphorus pentoxide tube to the gas reservoir R. The tube S led to another two-way tap U. One arm of U led to a mercury container W, and the other led through three phosphorus pentoxide tubes to the gas supply Z and the pumping system Y. The bulb V was inserted to catch any mercury which might inadvertently be let through the tap U.

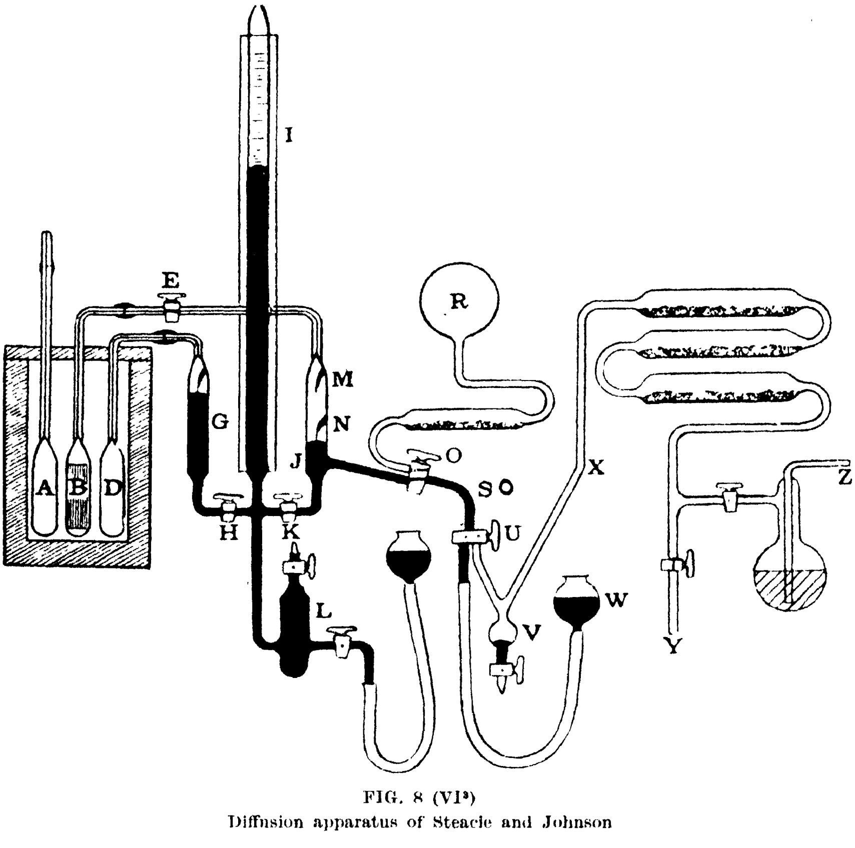

FIG. 8 (VI[3])
Diffusion apparatus of Steacie and Johnson

In carrying out an experiment, the bulb containing the silver was connected to the pumping system by means of the taps E, O, U, and Y, and the whole system was evacuated. The taps E and O were then closed. The tap U was turned so as to connect S with the mercury reservoir W, and the mercury was allowed to rise and fill the tube S. S was then connected to the gas reservoir R by means of the tap O, the mercury reservoir was lowered, and gas was drawn into S. O was next turned to connect S to the manometer tube J, and the mercury reservoir was raised, forcing the gas into J. The mercury was allowed to run up the tube after the gas till it took up the position shown in the figure. O was then closed and K opened, connecting J to the manometer. The mercury was brought to the lower pointer N and the pressure was read. Then, knowing the volume of the tube and the room temperature, the volume of the gas under standard conditions could be calculated.

The tap E was then opened and the gas was admitted to the bulb. The mercury level was brought up to M and the pressure read, after equilibrium had been reached. The absorption was then calculated from the difference between the calculated and the observed pressure.

The temperatures were measured by means of the ordinary type of constant-volume gas thermometer DGHI. The bulb D was filled with nitrogen. By means of the taps H and K, the same manometer was used for the absorption apparatus and the gas thermometer.

At the conclusion of an experiment the tap K was shut and E opened. The two-way tap O was turned so as to connect the tubes J and S, and the tap U so as to connect S to the mercury reservoir W. The reservoir was lowered and the mercury in J and S was allowed to run out. O, U, and Y were then turned to connect the bulb containing the silver to the pumping system. Prior to making an experiment, the furnace was raised to a temperature of about 550° in the case of the Pyrex glass apparatus, or 750° with quartz, and the bulb was evacuated continuously for 6 to 8 hours. The silver was allowed to stand *in vacuo* overnight, and the next morning the bulb was again pumped out for about an hour. The tap next to the bulb was then closed, and gas from the reservoir was admitted to the tube and measured as previously described. The gas was then let into the bulb, and after equilibrium had been reached the temperature and pressure were read. A series of observations was made without changing the gas. At high temperatures equilibrium was quickly reached, at temperatures around 200°, however, several days were required for equilibrium. At the conclusion of the experiment the bulb was again evacuated continuously for several hours, and the gas pumped out was collected and measured, and the volume compared with the volume originally admitted to the bulb. This long-continued pumping out is essential in order to obtain consistent results. The last traces of the gas are only very slowly removed from the silver.

Many modified types of this apparatus have been described, e.g. by Braun,[1] Bircumshaw,[2] Lobley and Jepson,[3] Chipman and Murphy,[4] Kruger and Gehm.[5] An account of all these methods is given by Smithells.[6]

Micro-diffusion and its application in analysis is discussed in Vol. II, p. 176–6·8.

Diffusion in Wood. A detailed study of the diffusion processes in woods (soft and hard) has been made by Burr and Stamm.[7] Four types of measurement were made in connexion with the investigation. The electrical conductivities of several species of woods saturated with salt solutions were determined. The ratios of these values to the conductivities of the solutions with which the samples were in equilibrium were assumed to be equal to the corresponding diffusion constants relative to unit dimensions of the wood. Direct measurements of relative diffusion constants were made in order to check the validity of this assumption. A series of microscopic measurements was made on a number of different species in order to determine to what extent certain of the structural dimensions differed from those taken by Stamm as typical of softwoods. Finally, measurements of the rate of transfusion of water vapour through wood and through regenerated cellulose were made, using the method of the steady state.

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[1] *Dissertation Anchen*, 1930.

[2] *Trans. Faraday Soc.*, 1935, *31*, 1439.

[3] *J. Inst. Met.*, 1926, *35*, 213.

[4] *Amer. Inst. Min-met. Eng. Tech. Pub.*, 591.

[5] *Annalen*, 1933, *16*, 174 and 190.

[6] *Gases and Metals, An Introduction to the Study of Gases*, Chapman & Hall, London, 1937.

[7] *J. Phys. Chem.*, 1947, *51*, 240.

Direct measurement of solute diffusion was made as follows: sodium chloride was allowed to diffuse from a concentrated solution into wood filled with water and the resulting salt concentrations at different depths were obtained by sectioning the wood in blocks and analysing for chloride ion volumetrically. The ends were dipped in a molten mixture of beeswax and rosin to minimize longitudinal diffusion and were then placed in a tall glass jar containing approximately 10 litres of 1·5 N sodium chloride solution. An electric stirrer was operated constantly. As each block was removed, 8 cm. of wood was cut from each end, and 3 cm. from each edge. The resulting block was then divided in half by a cut parallel to the longitudinal face, and from the two final blocks tangential sections were split off with a chisel so mounted as to ensure accurate sectioning. Each section was immediately placed in a flask with about 200 ml. of distilled water in order to remove the salt. The leaching process continued for two days or more at an elevated temperature and with occasional swirling of the flasks. The solution was then decanted and analysed for chloride. The wood sections were dried and weighed.

A step diagram was then constructed, the width of each step corresponding to the thickness of the section, and the height to the salt concentration in terms of grams per cubic centimetre of solution.

The mean external salt concentration for each block was determined by interpolating between the original and final concentrations of the brine, allowance being made both for the varying number of blocks in the solution and for the fact that the amount of salt absorbed varies as the square root of the time.

Theoretical distribution curves were calculated from the following formula:[1]

$$C/C_0 = 1 - 2/\sqrt{\pi}\int_0^{x/2\sqrt{Dt}} e^{-\beta^2}\, d\beta$$

where C = concentration of salt at any point within the wood,
C_0 = external salt concentration,
x = distance from the tangential face in centimetres,
D = diffusion constant in cm.^{2} per second, and
t = time in seconds.

The curve corresponding to a diffusion constant of $3{\cdot}36 \times 10^{-7}$ cm.^{2}/sec. fitted all the step diagrams with fair accuracy.

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[1] *Loc. cit.*

CHAPTER VII[3]

SOLUTION

SECTION 1: SOLUBILITY OF GASES IN LIQUIDS

HERE we may distinguish two cases:

(*a*) The solubility of slightly soluble gases such as oxygen or carbon dioxide.

(*b*) The solubility of very soluble gases such as hydrochloric acid or ammonia.

Method of Expression. The solubility of a gas in a liquid may be expressed in various ways:

1. The volume of the gas measured at the temperature and pressure of the experiment, dissolved in a given volume or mass of the solvent.
2. The volume of the gas corrected down to what it would occupy at 0° and 760 mm. pressure dissolved in a given volume or mass of the solvent.

When the volume of the solvent is 1 ml., the solubility expressed in either of these ways is called the absorption coefficient.

3. With more soluble gases, the mass of the gas dissolved in a given volume or mass of either solvent or solution may be used.
4. The solubility may be calculated as gram molecules of solute to gram molecules of solvent.

In order that comparisons shall be possible between solubilities expressed in these different ways, it is very desirable that in addition to a clear statement of the definition of solubility used, determinations of the densities of the solutions should also be given. Omission of the last determination frequently makes impossible the comparison of results of different experimenters.

The Preparation of Gas-free Solvent. The solvent to be used will first be purified by the ordinary processes and must then be freed from dissolved gases; as an example, we can take the preparation of air-free water. The dissolved air may be removed by boiling, by a reduction of pressure or a combination of both processes. A round-bottomed flask is fitted with a rubber stopper with a short glass tube passing through it, to which is fitted a short length of pressure tubing with a screw-clip. The flask is filled two-thirds full of water (distilled) and is boiled freely for 15 minutes; while it still boils the clip is closed and at the same time the flask is removed from the source of heat, so as to avoid a rise of pressure inside sufficient to blow out the stopper. The flask and its contents can then be cooled under the tap. Or a distilling-flask containing the distilled water can be closed with a rubber stopper and connected by means of rubber tubing and a clip to a good water pump. Nearly all the air will have been removed in half an hour and if necessary the removal can be accelerated by warming the flask: in the latter case a reflux condenser can be fitted between the flask and the pump. The clip is of course closed before the pump is stopped.

Determination of the Solubility of Slightly Soluble Gases. The apparatus as shown in Fig. 1 (VII^3) consists of an absorption pipette A, a measuring-tube B, and a levelling-tube C, fitted by means of clips to a stand which conveniently has a scale between B and C to enable experiments to be made at pressures other than atmospheric; *a* is a single-way tap and *b* and *c* are three-way taps. A and B are sometimes connected with metal tubing and sometimes with thick-walled rubber tubing. The measuring-vessel B is graduated in millilitres and is filled with mercury. The tap *a* is connected to the vessel containing the gas-free solvent, by means of the rubber tube, and is kept opened. The three-way tap *c* is connected to the pump and A is exhausted. By opening the clip and tilting the vessels, A may now be filled with gas-free solvent and the taps *a* and *c* are then closed. The capillary above B is next connected to the gas supply and *c* and *b* are opened so that the tube is filled with the gas; by closing first *b* and then *c* this will be at atmospheric pressure when the pump is off. Tap *b* is turned so that gas enters the measuring-tube B, where it is saturated with water vapour by means of a drop of water previously introduced above the mercury. Tap *b* is closed and the mercury in B and C levelled. After standing for 10 minutes, the temperature, volume, and pressure of the gas in B are read. A and B are now connected, C is raised, and 20 ml. of solvent run out of *a* into a 20-ml. flask. The tap *a* is closed and the apparatus gently shaken to hasten the absorption of the gas. C and B are levelled and the apparatus is again shaken. If the level in B is altered, C must be again adjusted and shaking repeated until it is found that no further absorption occurs. Again allow to stand for 10 minutes and read off the temperature, volume, and pressure of the gas in B. If the temperature and pressure are the same for both the volume measurements, the volume of gas absorbed is $V_1 - V_2 - 20$. The volume of solute is now found by running it out into a measuring vessel. The volume of solute run out in the first

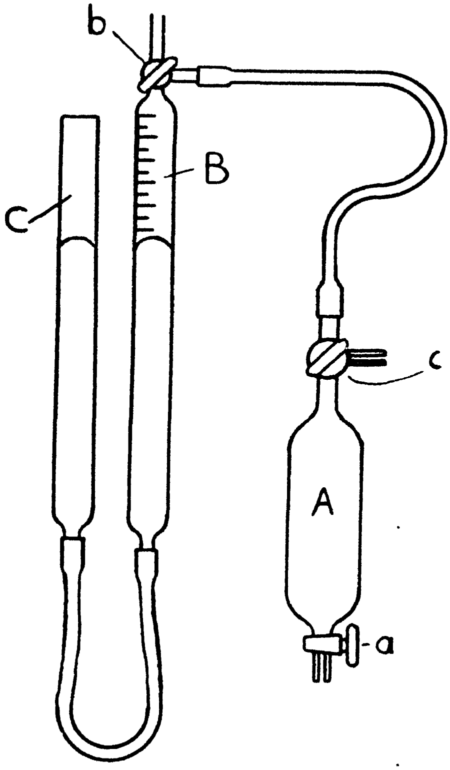

FIG. 1 (VII^3)
Gas absorption apparatus

instance (taken above as 20 ml.) can be determined more accurately by weighing (making allowance for what is left in the capillary below the tap a), and the same applies to the volume of the solution. The volume of gas absorbed is measured as a moist gas at temperature t and pressure p and can be corrected down to dry gas at 0° and 760 mm. In case the barometric pressure and the temperature have altered during the experiment, the volumes v_1 and v_2 will be corrected down to dry gas at 0° and 760 mm. before subtracting. The same apparatus can be used for measuring the solubility at different temperatures where A alone is placed in the thermostat, and for pressures other than atmospheric. In the general case

Let V = volume of solvent remaining in A
x = volume of solvent run out of A
y = volume of gas in B at the start, measured at temperature $T°$ K, pressure P mm. and aqueous vapour pressure f
z = volume of gas in B at the end, measured at temperature $T_1°$ K, pressure P_1 mm. and aqueous vapour pressure f_1
T_2 = the temperature of A on the absolute scale
f_2 = the vapour pressure of the solvent at $T_2°$ K

Then the volume of dry gas at the start is :

$$\frac{y(P-f)273}{T.760}$$

The volume of dry gas in B at the end is :

$$\frac{z(P_1-f_1)273}{T_1.760}$$

The volume of dry gas in A at the end is :

$$\frac{x(P_1-f_2)273}{T_2.760}$$

Therefore the absorption coefficient at temperature T and pressure P is :

$$\frac{273\left\{\frac{y(P-f)}{T}-\frac{z(P_1-f_1)}{T_1}-\frac{x(P_1-f_2)}{T_2}\right\}}{V.760}$$

The dimensions of the apparatus must obviously be chosen with due regard to the solubility of the gas being measured. With a gas such as oxygen, a large absorber and a narrow measuring tube are necessary. In the case of a number of gases which are only slightly soluble, such as oxygen and carbon dioxide, suitable analytical methods are available for the determination of the amount of gas present in the solution and in such cases more accurate results are obtainable by this means than by the direct measurement of the volume of gas dissolved.

Solubility of Oxygen in Water. As an example we may take the determination of the solubility of oxygen in water. Measurements of this quantity have been made by Winkler and Whipple. The latter forced the gas through 3 litres of water and took samples from time to time ; he found that several hours were sometimes required to reach saturation. A 3-litre bottle filled with distilled air-free water is placed in the thermostat, and purified oxygen is bubbled through. Samples are taken in a 250-ml. narrow-necked bottle fitted with a glass stopper. In taking the sample, the glass stopper is replaced by a rubber stopper with a delivery tube extending to the bottom of the bottle and an exit tube passing to the bottom of the stopper only: the sample is drawn into the bottle by suction and at least one bottle-full in excess is drawn through to avoid disturbance of the equilibrium due to the air in the bottle at the start. The glass stopper is then placed in the bottle and the sample is ready for the determination. The solutions required are:

(*a*) 48 grams of manganous sulphate dissolved in water and made up to 100 ml.

(*b*) hydrochloric acid solution, specific gravity 1·18

(*c*) 70 grams of potassium hydroxide and 15 grams of potassium iodide dissolved in water and made up to 100 ml.

(*d*) N/40 sodium thiosulphate solution standardized against N/40 potassium bichromate solution

(*e*) freshly prepared starch solution

The alkaline potassium iodide solution precipitates manganous hydroxide, and this on acidifying with hydrochloric acid liberates an equivalent quantity of iodine which is titrated with the standard thiosulphate.

The glass stopper is removed from the sample, and by means of a 1-ml. pipette this quantity of manganous sulphate is added. The pipette is lowered to the bottom of the bottle before the solution is allowed to run out; 1 ml. of the alkaline iodide solution is then added in the same manner and the glass stopper inserted (whereby 2 ml. of water are forced out and no air bubble is left in the bottle).

The bottle is then turned until the contents are thoroughly mixed and allowed to stand until the precipitate settles; 1 ml. of hydrochloric acid is now added in the way described above, the stopper is again replaced, whereby 1 ml. of the supernatant liquid is forced out, and the contents are well mixed; 200 ml. of the contents are now transferred to a flask and titrated with the N/40 thiosulphate, adding a few millilitres of the starch solution when the solution has become a faint yellow. The number of millilitres of thiosulphate used gives the solubility in milligrams per litre. In very accurate work the corrections for the 2 ml. of water forced out when the stopper is replaced after the addition of the manganous sulphate and the alkaline iodide solutions may be applied. Observations of the temperature and barometric pressure at which the solution was saturated are of course recorded.

When it is desired to determine the solubility of a gas at pressures less than atmospheric this can conveniently be done by diluting the gas with another, e.g. if air be used in the above experiment at a total pressure of 760 mm., the oxygen, being 20·8 per cent of the mixture, is under a partial pressure of $0{\cdot}208 \times 760 = 158{\cdot}1$ mm. and the solubility of the oxygen measured is that of oxygen under this pressure.

Determination of the Solubility of very Soluble Gases. All the very soluble gases are either acid in solution, such as sulphuretted hydrogen and sulphur dioxide, or alkaline, such as ammonia, so that suitable analytical methods are always available. Suppose the solubility of hydrochloric acid gas in water is to be measured. A thin-walled glass vessel of the shape shown in Fig. 2 (VII³) is first cleaned, dried and weighed; it is then filled with water and weighed again to find its volume. About 15 ml. of distilled water are placed in the bulb so that it is half full and the apparatus is placed in the thermostat: a slow current of the gas is then passed through the arm *a* and is allowed to pass until the water is saturated, the arm *a* is then sealed off and finally the arm *b*. The tube is then carefully dried and weighed, thus giving the weight of the solution. File marks are made above and below the bulb, which is placed in a strong beaker containing 300 ml. of N sodium hydroxide solution and with the aid of a glass rod is broken to pieces while the bulb is well below the liquid. The excess of alkali is then titrated with normal hydrochloric acid. A sample of the saturated solution prepared in a similar way at the same time is used for a density determination; the weight of solution used in the solubility determination is known and its volume can now be calculated, and knowing the volume of the whole tube a correction can be applied to the solubility for the volume of the hydrochloric acid gas above the solution.

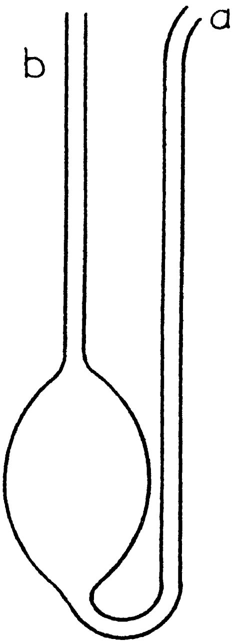

FIG. 2 (VII³)
Thin-walled glass vessel for gas solubility determination

The absorption coefficient of a gas (*K*) is the volume of gas (in millilitres) calculated at N.T.P., absorbed by 1 ml. of the liquid at a given temperature when the partial pressure of the gas is 760 mm. The following table gives the solubility of a number of gases in water at 20°:

Gas	K
Hydrogen	0·0184
Helium	0·0138
Nitrogen	0·016
Oxygen	0·0314
Argon	0·037
Carbon monoxide	0·0232
Carbon dioxide	0·878
Methane	0·0331
Ethane	0·0472
Ethylene	0·122
Ammonia	715·4
Nitrous oxide	0·63
Nitric oxide	0·047
Hydrogen sulphide	2·67

SECTION 2: SOLUBILITY OF LIQUIDS IN LIQUIDS

When two liquids are shaken together they may be (*a*) miscible in all proportions, (*b*) immiscible, (*c*) partially miscible. The latter case alone concerns us. The diffusion of one liquid into another is considered on p. 131. In the case of partially miscible liquids we may get one phase or two present, depending on the proportions of the two substances in the mixture. When two phases are present, the one having the lower density will float on the top of the other and each phase will be a saturated solution, one of A in B and the other of B in A. When a single phase is present it will in general be an unsaturated solution. Two methods are in use for determining the solubilities, ' the analytical method ' and the ' synthetic method '.

Solubility of Phenol in Water. As an illustration we may take the determination of the solubility of phenol in water.

Analytical Method. In the analytical method, 250-ml. bottles with glass stoppers are used; 60 grams of phenol and 120 grams of water are placed in the bottle, the stopper put in position and, if desired, a rubber cap can be tied over the stopper and neck of the bottle. The bottles are placed in the thermostat and shaken for 2 hours. The shaking is stopped, the bottles are placed in a vertical position with the stoppers only projecting and allowed to stand until the two layers have separated out. 10 ml. of the upper layer are removed by means of a pipette, transferred to a stoppered conical flask and weighed, and the amount of phenol present is determined by the use of a standard bromine solution by the method of Koppeschaar. The bottle is then closed and shaken for another hour, after which another 10 ml. of the top layer is taken for analysis. This process is continued until two successive analyses agree, showing that the top layer, and by inference the bottom layer, are both saturated. 10 ml. of the bottom layer are now removed and analysed in a similar way; the finger is placed over the top end of the pipette and the lower end is introduced into the lower layer; the finger is then removed and the liquid drawn up. After removing the pipette, the outside is carefully dried to remove any adhering portions of the upper layer which might drain down, and the liquid examined to see that none of the upper layer is present; if this is found to be satisfactory the solution can be weighed and analysed. Further experiments are conducted in the same manner at other temperatures. The method of analysis used will of course depend on the nature of the two liquids and must be chosen to meet each individual case. In some cases physical methods may be found to be the most suitable, or it may happen, when their boiling-points are widely different, that one liquid can be evaporated off from the other. Again the amounts of the substances to be added in the first instance must be determined by experiment; equal quantities generally will be tried first and it may then be found that one liquid goes completely into solution in the other or that there is only a small quantity of one layer—in this case more of the deficient substance must be added and shaking resumed until the amounts of each of the two layers are sufficient for examination.

Synthetic Method. In the synthetic method a number of soft glass tubes are prepared and the phenol and water are weighed out into these in a series of approximate ratios 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, 7/3, 8/2, 9/1, and the tubes are then sealed up. One of the tubes is now taken and heated with shaking until the contents become homogeneous ; it is then placed in a large bath of water at this temperature and the bath is allowed to cool slowly. Suddenly an opalescence will appear in the tube, and the temperature of the bath is noted : the opalescence is due to the appearance of the two phases, solution of B in A and of A in B. It is possible to get the temperature at which the opalescence appears on cooling much more exactly than that at which the two phases disappear on heating. The temperature and the composition of the mixture are now plotted as one point on the solubility curve. When all the values have been plotted the gaps in the curve will be apparent and the mixtures having approximately the composition required can be made up and the solution temperatures may be determined.

Continuous Liquid-liquid Extraction. For use with immiscible solvents the apparatus of Palkin, Murray and Watkins [1] can be used. The solvent is conveyed to the bottom of the solution being extracted from where it rises through the solution and returns to the boiling-flask. In the apparatus of Matchett and Levine,[2] a sintered glass plate used to distribute the solvent is permanently sealed in the extraction tube where it covers the entire cross-section and is protected from breakage. Solvent is distributed throughout the entire volume of the solution being extracted, rather than in a narrow stream of droplets. The apparatus somewhat resembles an ordinary Soxhlet with a long narrow funnel filling the centre compartment and the stem passes through the plate near the bottom of the thimble vessel.

Liquid-liquid Extraction Data

The study of this method of extraction has largely developed from the work of Othmer and his co-workers and the following account of liquid-liquid extraction is due to them.[3]

Considerable data of a physico-chemical nature are necessary for the development of liquid-liquid extraction processes and the design of equipment for them. A knowledge of the phase equilibrium relations (mutual solubility, distribution characteristics, and concentration characteristics) for the constituents involved allows the prediction of the applicability of the process and permits a mathematical treatment of the extraction methods that may be used.

A liquid-liquid extraction process is concerned with at least three liquids and is based on the transfer of one liquid, the solute, from a solution in a first liquid phase to another liquid phase in order to bring about any one of several effects. To avoid confusion, the liquid in which the solute is originally present will be termed the 'diluent' and the other liquid will be termed the 'solvent'. The diluent and the solvent are, of necessity, practically insoluble in each other. The solute, however, in the usual case (the only one considered here) is completely miscible with both the diluent and the solvent; and when added to a two-phase mixture of the two, it distributes itself in accordance with some partition law. The presence of the solute increases the solubility of the diluent in the solvent and of the solvent in the diluent. The driving force causing an extraction process to proceed is measured, as with any diffusion process, by the distance the system is from equilibrium. The difference between the actual concentration of solute in one phase and the concentration which would be in equilibrium with that of the other phase is the force tending to dissolve (or release from solution) the solute. The algebraic sum of these differences of concentrations causes the process to go forward. Obviously, the extraction may proceed in either direction; and the terms 'diluent' and 'solvent' have to adjust themselves, depending on the operation in question.

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[1] *Ind. Eng. Chem.*, 1925, *17*, 612.

[2] *Ibid.*; *Anal.*, 1941, *13*, 264.

[3] *Ind. Eng. Chem.*, 1941, *33*, 1240.

The solubility-composition relations of a three-component system are usually represented graphically on a triangular diagram. These systems are of importance since extraction processes involving them are used industrially and are the bases of many patents and technical applications.

SECTION 3: SOLUBILITY OF SOLIDS IN LIQUIDS

A discussion on the solubility of solids is given by Hulett and Allen.[1] They point out that the solubility of small particles is greater than that of a plane surface. In the case of gypsum it was found possible to prepare solutions containing 20 per cent more solute than a normal saturated solution, i.e. one in equilibrium with a plane surface, by shaking with particles having a diameter of 0·3 micron. Even plates of gypsum when vigorously stirred with water gave a solubility 5 per cent too high owing to the ease with which the crystals break up to fine powder, and normal results were only obtainable by rotating the water over the gypsum plates by means of a stirrer working at 50 revolutions per minute. Using a fine powder and gentle stirring a high solubility was first obtained and then as the fine particles went into solution and the larger ones increased in size the solubility dropped to the normal value, but the process is a slow one and equilibrium was not reached for five days. They also point out the necessity for density determinations, since results are variously expressed as:

(*a*) Grams of solute in 100 grams of solvent
(*b*) Grams of solute in 100 grams of solution
(*c*) Grams of solute in 100 ml. of solution
(*d*) Gram molecules of solute in 100 gram molecules of solvent

In order to make certain that equilibrium has been reached it is best to approach it from both sides—in one case by stirring the solid with the solvent and in the other by stirring a supersaturated solution with the solid. Since in most cases the solubility of a solid increases with rise of temperature the supersaturated solution is prepared by heating the powdered solid with water at a higher temperature than that of the determination for a short time, say 20 minutes.

Method of Agitating Solutions. The necessary agitation can be secured by means of the arrangement described by Noyes, shown in Fig. 3 (VII^3), where the bottles act as stirrers in the thermostat. The bottles are of about 500 ml. capacity and are steamed out before use. The solid, consisting of some large particles and a quantity of fine powder (which goes into solution more quickly owing to its surface area), is placed in two of the bottles together with the distilled water or other solvent to fill them three-quarters full. In the other two bottles a few large particles of the solid and supersaturated solution are placed. The flat-topped glass stoppers are inserted and if desired a small rubber cap is tied over them. The bases of the bottles fit into recesses in the central wooden disk *a* and the end disks *b* are then rotated along the screw until they press against the stoppers and hold the bottles in position. The disks *b* are fixed by means of the metal nuts shown. Another method consists in fixing a conical flask or a large tube 25 by 2·5 cm.

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[1] *J. Amer. Chem. Soc.*, 1902, *24*, 667.

in a vertical position, closing the neck with a rubber stopper through which passes a glass tube extended to a flat piece at the top which acts as a guide and bearing for the rod of a glass stirrer.

Soluble substances generally go into solution more readily than slightly soluble ones, and in general 4 hours' stirring will be sufficient for equilibrium to be set up : with less soluble substances this time may be extended to days.

Method of Procedure. After 4 hours the stirrer is stopped and the bottles removed and hung in the thermostat with their necks projecting from the water ; when the solid has subsided the clear solution is ready for removal. When the tube form of apparatus is used, a second hole is sometimes bored in the rubber stopper and a short piece of glass tube fitted in it through which the pipette can be inserted for the removal of the solution ; this tube is stoppered during the stirring. Various forms of apparatus have been devised for the removal of the solutions ; in all cases the latter is filtered to avoid the introduction of minute particles of suspended solid. Lowry used the tube shown in Fig. 4 (VII^3), the end of which is covered with two thick sheets of filter paper and a layer of linen held in place by a rubber band. The tube is warmed to the temperature of the bath and lowered into the solution, which filters in ; the tube is then quickly removed and its contents poured into the weighing-vessel. Again a small 25-ml. Sprengel pyknometer with glass caps can be used. The pyknometer is weighed and its end fitted with a piece of rubber tube holding a piece of glass tubing plugged with cotton-wool. The solution is drawn up to the mark with the pyknometer in the thermostat, the caps put on and the density determined. The contents of

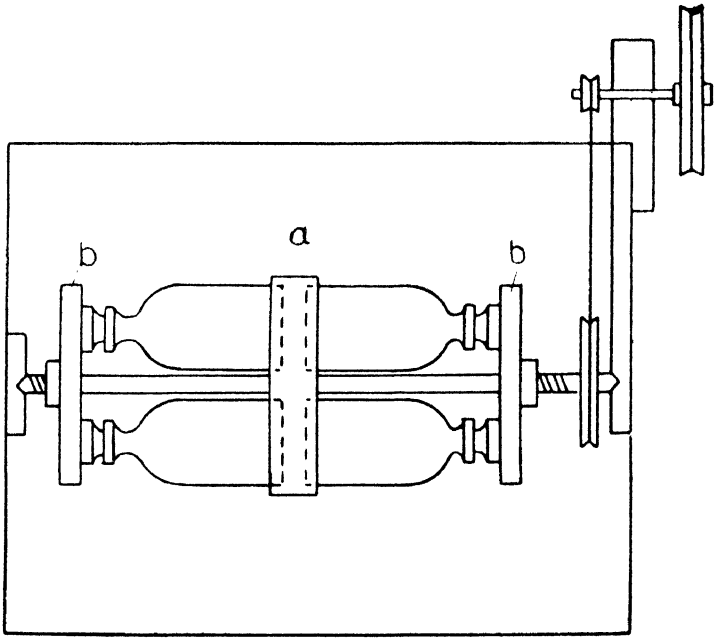

FIG. 3 (VII^3)
Noyes' apparatus

the tube are then washed out with solvent. Another pipette for the same purpose is shown in Fig. 5 (VII³). The stop-cock *f* is attached to the graduated end of the pipette with rubber tubing, and the filter tube *e*, containing cotton-wool, is attached to the lower end. With both taps open the solution is drawn up until it reaches the graduated part of the tube: the upper tap is then closed, the pipette removed from the solution, the lower tap closed, the connexions *e* and *f* removed, and a rubber cap placed over the open end *b*. Any solution in the capillary below the tube is removed by means of a filter paper and the pipette and its contents are weighed. If the pipette has been previously calibrated with water, the density can be determined and the contents can be washed out completely with solvent.

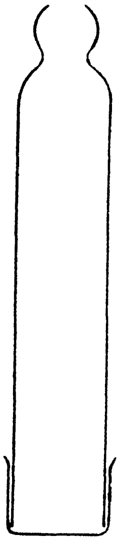
FIG. 4 (VII³)
The Lowry tube

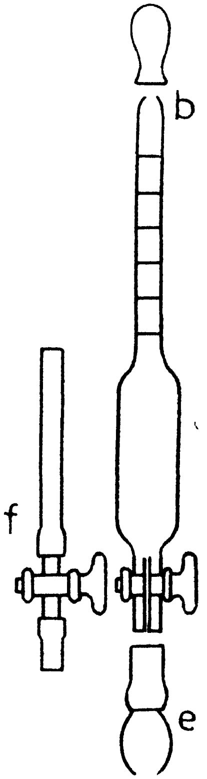

FIG. 5 (VII³)
Density pipette

Evaporation of Solutions. When the dissolved substance is stable the weight of it present in a known weight of solution is found by evaporation. Great care must be used to avoid loss by spattering; with aqueous solutions evaporation on the water bath is used, covering the dish with a large condensing funnel to prevent dust falling in. Deep evaporating basins with flat bases and made of thin glass with glass covers are convenient. After evaporating to dryness the dishes are heated to constant weight in the air oven at 110°. If the densities and solubilities for all four samples agree, it may be taken that equilibrium had been reached and the solubilities are correct. In case of disagreement a further period of stirring must be used. A form of apparatus specially devised for the purpose is the Liebig drying tube shown in Fig. 6 (VII³). As shown, this has a loosely fitting draught tube C between which and the drying tube a strip of filter paper is placed to prevent solvent condensed in C running back on to the solid. This form was also used in Ostwald's laboratory by Trevor. The form of the tube is intended to avoid loss by spurting. T. W. Richards evaporated his solutions in small quartz flasks in an electric oven at 103°. The flasks had long necks and a tube passed down the neck to 4 cm. above the surface of the solution; dry air was passed down the tube and the tube and flask were weighed together. Substances which are not stable to heat may be determined in some cases by chemical analysis and in others by making use of some physical property. The latter is often very convenient when a large number of determinations have to be made. If a dipping refractometer is available, this may be most useful; or the electric conductivity can be used, or the density of the solutions. In either case the first step is to make up a series of solutions of known strength and measure the physical property in question for these solutions. Then, when the composition of an unknown solution has to be determined, the property in question is measured for this solution or for a given weight of this solution diluted with a known weight of solvent ; referring to a large-scale curve the composition of the diluted solution can be obtained and from this, that of the undiluted one calculated.

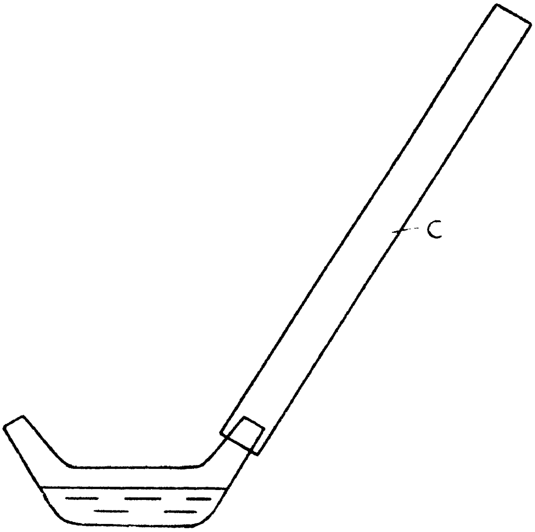

FIG. 6 (VII^3)
Liebig drying tube

Flotation Equilibrium. In this connexion the method of floating equilibrium is very convenient. Floats of the capacity of 5 ml. and the shape shown in Fig. 7 (VII^3) are used ; these are made of glass and weighted with mercury, the weight being finally adjusted by sealing bits of glass on one end. They float or sink with a density change of 2×10^{-7} corresponding to 0·002 per cent of sodium chloride. Small beads of known specific gravity can also be purchased from makers of hydrometers and used when less accuracy is desired. Solutions are prepared in which the float sinks and solvent is added until the float just rises. The temperature is recorded and the solution analysed. A beaker and the float are weighed, the solution to be determined is added and the weighing repeated, solvent is then added with stirring (the temperature of the original determination being maintained) until the float rises. The beaker and its contents are weighed again. The degree of dilution is thus known and the diluted solution has the same composition as the original solution.

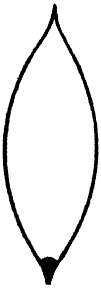

FIG. 7 (VII^3)
Glass float for flotation-equilibrium experiments

In the case of very slightly soluble salts such as silver chloride, the methods described above are unsuitable. In such cases the electrical conductivity of the solution can be used to measure the concentration. The requirements of the method are that the saturated solution shall be so dilute that the equivalent conductivity may be taken to be the same as the conductivity at infinite dilution, and yet this equivalent conductivity must be much greater than the specific conductivity of water. For example, a solution of silver chloride saturated at 18° had a specific conductivity $2{\cdot}4 \times 10^{-6}$ reciprocal ohms, that of water at the same temperature being $1{\cdot}16 \times 10^{-6}$ ohms.

Given that

$$\begin{aligned} \lambda_\infty \mathrm{KCl} &= 131{\cdot}2 \\ \lambda_\infty \mathrm{AgNO_3} &= 116{\cdot}5 \\ \lambda_\infty \mathrm{KNO_3} &= 126{\cdot}1 \\ \lambda_\infty \mathrm{AgCl} &= \lambda_\infty \mathrm{AgNO_3} + \lambda_\infty \mathrm{KCl} - \lambda_\infty \mathrm{KNO_3} \\ &= 116{\cdot}5 + 131{\cdot}2 - 126{\cdot}1 \\ &= 121{\cdot}6 \end{aligned}$$

Now K due to $AgCl + H_2O = 2{\cdot}4 \times 10^{-6}$ ohms^{-1} per ml.

K due to $H_2O = 1{\cdot}16 \times 10^{-6}$ ohms^{-1} per ml.

∴ K due to $AgCl = 1{\cdot}24 \times 10^{-6}$ ohms^{-1} per ml.

Or for 1,000 ml. with electrodes 1 cm. apart $1{\cdot}24 \times 10^{-3}$ ohms^{-1}

∴ Number of molecules per litre of AgCl

$$= \frac{1{\cdot}24 \times 10^{-3}}{121{\cdot}6} = 1{\cdot}02 \times 10^{-5}$$

Another method consists in measuring the E.M.F. of a cell, e.g.

$$\mathrm{Ag} \mid \frac{\mathrm{N}}{10}\mathrm{AgNO_3} \mid \mathrm{KNO_3} \mid \frac{\mathrm{N}}{10}\mathrm{KCl} \text{ saturated with } \mathrm{AgCl} \mid \mathrm{Ag}$$

The E.M.F. at 25° was 0·45 volt, the fraction of $AgNO_3$ dissociated in N/10 solution is found from the conductivity to be 0·82.

$$\text{Now } E = \frac{0{\cdot}0002T}{n_c} \log \frac{c_1}{c_2}$$

$$\therefore \log \frac{c_1}{c_2} = \frac{0{\cdot}45}{0{\cdot}0002 \times 298} = 7{\cdot}55$$

$$\therefore \frac{c_1}{c_2} = 3{\cdot}548 \times 10^7$$

$$c_1 = 0{\cdot}82 \times \frac{1}{10} \text{ gram molecules per litre}$$

$$\therefore c_2 = \frac{0{\cdot}082}{3{\cdot}548 \times 10^7} \text{ gram molecules per litre}$$

$$= 2{\cdot}31 \times 10^{-9} = C_{Ag}$$

Now N/10 KCl is 0·85 per cent dissociated.

$\therefore C_{Cl} = 0{\cdot}085$ molecules per litre.

$$\begin{aligned} \therefore C_{Ag} \times C_{Cl} &= 2{\cdot}31 \times 10^{-9} \times 0{\cdot}085 \\ &= 1{\cdot}96 \times 10^{-10} \end{aligned}$$

In solutions containing silver chloride only

$C_{Ag} = C_{Cl} = C_{AgCl} = \sqrt{1{\cdot}96 \times 10^{-10}} = 1{\cdot}4 \times 10^{-5}$ molecules per litre.

Determination of Trace Metal Ions by Chemical Means. A very useful reagent is provided by diphenylthiocarbazone [1] (dithizone). According to Kolthoff, Perlich, and Weiblen [2] it can be used at extremely great dilutions without evaporation and using only small amounts of solvent. They claim that it has advantages over electrometric methods as the total amount of dissolved (ionized and un-ionized) metal is determined. The electrical conductance method is limited in its application and allows only the determination of the ionized part of the solution. The potentiometric method has a wider range of application than the conductometric one, but it allows only the determination of the activity of the metal ion of the dissolved salt. The activity coefficient of the dissolved metal ion has to be known in order to find the concentration of the latter. Moreover, the concentrations of undissociated salt or of complex metal ions are not determined by the potentiometric method. One estimation by Kolthoff and his colleagues [3] will be recorded, namely the solubility of lead chromate in water. The lead in a saturated aqueous solution of pure lead chromate was determined in 50 ml. of the clear centrifugate. The solubility found was $5{\cdot}3 \times 10^{-7}$ M, (M = mols per litre) in fair agreement with the data of Kohlrausch and Rose [4] ($6{\cdot}2 \times 10^{-7}$ M) and of Kohlrausch [5] ($3{\cdot}1 \times 10^{-7}$ M). These authors used the conductance method. Hevesy and Paneth,[6] using a radioactive method, found a solubility of $3{\cdot}7 \times 10^{-8}$ M while Hevesy and Rona,[7] using a similar method, found a solubility of 2×10^{-7} M.

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[1] Fischer, *Angew. Chem.*, 1929, *42*, 1025; 1934, *47*, 685.

[2] *J. Phys. Chem.*, 1942, *46*, 561.

[3] *Loc. cit.*

[4] *Z. physik. Chem.*, 1893, *12*, 241.

[5] *Ibid.*, 1903, *44*, 197.

[6] *Z. Anorg. Allgem. Chem.*, 1913, *82*, 323.

[7] *Z. physik. Chem.*, 1915, *89*, 305.

SECTION 4: PARTITION COEFFICIENTS

The Law of van 't Hoff[1] **or Henry.** This law states that if a substance has the same molecular weight in the gaseous and dissolved states, its partial pressure in the vapour is proportional to the concentration in the solution. It can be shown that if the vapour is in equilibrium with separate solvents the ratio of the concentrations of the two solvents will be constant. If the two solvents are immiscible then we have a constant ratio of concentration in the two solvents as long as the molecular weight of the solute is the same in both. This is the partition law. When the concentrations in the two solvents have their maximum values each of the solutions is saturated and we have

$$\frac{C_a}{C_b} = r = \frac{S_a}{S_b}$$

where C_a and C_b are the concentrations of the solute in the solvents a and b, r is the constant ratio, and S_a and S_b are the solubilities of the solute in the solvents a and b. This equality has been proved by Jakowkin, for the distribution of iodine between water and carbon tetrachloride and a number of other solvents. When the solvents are not completely immiscible, as in the case of ether and water, the relationship will not hold so exactly because S_a and S_b will now represent the solubilities of the solute in a saturated with b and in b saturated with a, and at other dilutions the amount, for example, of b required to saturate a will be modified by the presence of the solute.

Wider Application of Law. Nernst has extended the principle to those cases where chemical reaction takes place between the different molecular species. For example, if a substance undergoes partial electrolytic dissociation in one solvent but not in the other we get a constant ratio between the concentrations of the still undissociated molecules in the two solvents; thus succinic acid is slightly dissociated in water but not in ether, and we get a constant ratio between the total concentration in the ether and the concentration of the undissociated fraction of the acid in the water.

Example of the Determination of the Partition Coefficient. As an example of the use of a substance which has a normal molecular weight in both solvents, the partition of iodine between water and carbon tetrachloride studied by Jakowkin will be taken. At 25° the solubilities are 0·3395 gram in 1 litre of water and 30·33 in 1 litre of saturated carbon tetrachloride, i.e. saturated solutions are roughly N/400 and N/4; therefore 200 ml. of the former would require 25 ml. of N/50 thiosulphate, while 10 of the latter would require 25 ml. N/10 thiosulphate.

Taking three 500-ml. bottles with glass stoppers, we place 100 ml. of carbon tetrachloride and 300 ml. of water in each and 3, 2, and 1 grams of iodine respectively. The stoppers are put in and rubber caps secured over the stoppers and necks and the bottles are shaken in the thermostat for 2 hours. At the end of that time they are removed from the shaker and fixed vertically for the two layers to separate; with the present solutions this occurs quickly, but some solutions take hours to clear up.

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[1] So called by Nernst.

10 ml. of the lower carbon tetrachloride solution are then removed with a pipette, avoiding inclusion of any of the upper layer. This can be done by placing the moistened forefinger of one hand over the end of the pipette and grasping the bulb with the other hand just before putting the point in the solution. The warmth of the hand expands the air in the pipette so that small bubbles escape while it passes through the upper layer. 10 ml. are then sucked up, the pipette removed, the outside wiped, and the solution is titrated with N/10 thiosulphate after the addition of water. The bottles are re-stoppered, shaken again for an hour, and another 10 ml. are withdrawn and titrated, and so on until constant results are obtained; 200 ml. of the top layer are then titrated with N/50 thiosulphate. Jakowkin obtained such results as the following:

Grams of iodine per litre of CCl_4 solution	Grams of iodine per litre of water solution	$\frac{C_1}{C_2}$
8·5	0·10	85·0
17·5	0·20	87·5
30·3	0·34	89·2

The Distribution of an Acid between Two Solvents in one of which it Dissociates. Chandler's experiments with succinic acid between ether and water may be taken as an example. Succinic acid is purified by recrystallization from distilled water. The ether is shaken with dilute sodium hydroxide solution, washed repeatedly with distilled water and then distilled; the middle portion of the distillate is used or Werner's method of shaking with silver hydroxide may be used. A stock solution of succinic acid containing 20 grams per litre is made up and is diluted as required; e.g. dilutions of 1·5, 10, 25, and 100 might be used. Equal volumes, say 200 ml., of the ether and the aqueous acid solution are shaken together in the thermostat in the usual way, allowed to stand for half an hour, and then a sample of the aqueous solution is removed for analysis, the glass pipette bulb being warmed by the hand and its tip passed through the ether layer. The process is repeated until a constant value is obtained, when a sample of the ether layer is also analysed. N/10 barium hydroxide is used for the more concentrated solutions and N/50 for the more dilute; the indicator is phenolphthalein. Before titrating the ethereal solution, water is added and the ether is distilled off.

Method of Calculation. Let k_1 be the primary ionization constant of the acid.

Let A be the molecular concentration of the aqueous layer
α be the degree of ionization of the aqueous solution
p be the ratio: total concentration of the acid in aqueous solution to concentration of acid in the ether solution

P be the true partition coefficient; e.g. the ratio of the concentration of the undissociated acid in the aqueous layer to the concentration of the acid in the ether layer

Then α can be calculated from the dilution law, $\frac{\alpha^2}{(1-\alpha)V} = k_1$ and P from the relation $P = p(1-\alpha)$.

Some results obtained by Chandler for succinic acid at 25° were:

$$k_1 = 66{\cdot}5 \times 10^{-6}$$

A	100α	p	P
0·1708	1·9	7·73	7·59
0·0287	4·7	7·73	7·36
0·0120	7·2	7·95	7·37
0·0039	12·2	8·42	7·39
0·0023	15·6	8·79	7·42

Further Example. Nernst's principle can also be applied to the case when the substance is associated in one of the solvents and dissociated in the other. Dawson's results for the distribution of acetic acid between water and chloroform illustrate the case. Here the acid is associated in the chloroform and dissociated in the water. The strongest aqueous solution of acetic acid used was approximately 1·8 normal, other solutions being prepared by diluting this down to ten times; 60 ml. of the solution and 60 ml. of the chloroform were placed in a cylindrical separating funnel and immersed in a thermostat, with the exit end projecting to keep it dry. At intervals of 5 minutes for a period of 0·75 hour the funnel was removed and violently shaken by hand. The two phases were allowed to separate in the thermostat for 0·5 hour, and the two layers were then run off into separate stoppered tubes for analysis. N/4 and N/40 solutions of caustic soda free from carbonate were used for the titrations.

Method of Calculation. Let C_1 and C_2 represent the total acid concentrations in the water and chloroform respectively.

Let α be the dissociation fraction in the water solution.

Then $C_1(1-\alpha)$ is the concentration of undissociated acid in the water.

If r is the distribution ratio for simple molecules of the acid between water and chloroform, $\frac{C_1(1-\alpha)}{r}$ is the concentration of the simple molecules of acid in the chloroform and $C_2 - \frac{C_1(1-\alpha)}{r}$ that of the double molecules. Then from the Law of Mass Action:

$$\frac{\left\{\frac{C_1(1-\alpha)}{r}\right\}^2}{C_2 - \frac{C_1(1-\alpha)}{r}} = K_1 = \frac{C_1^2(1-\alpha)^2}{r^2C_2 - rC_1(1-\alpha)}$$

The dissociation constant K for acetic acid at 25° is $1{\cdot}8 \times 10^{-5}$, hence the values of α can be calculated for each dilution from Ostwald's dilution formula $\frac{\alpha^2}{(1-\alpha)V} = K$. From any pair of experimental results we can now calculate a value for r: using the second and fifth experiments shown below, the value of r is found to be 42·9, and having obtained this we can get K_1. A few of Dawson's figures will illustrate the results obtained :

C_1	C_2	$C_1(1-\alpha)$	$\frac{C_1(1-\alpha)}{r}$	$C_2 - \frac{C_1(1-\alpha)}{r}$	K_1
1·535	0·2277	1·530	0·03565	0·1920	0·0066
0·9084	0·08904	0·9048	0·02109	0·06795	0·0065
0·6089	0·04557	0·6052	0·01411	0·03146	0·0063
0·2696	0·01222	0·2675	0·006234	0·005986	0·0065
0·1946	0·007586	0·1929	0·004495	0·003091	0·0065

The calculations are based on the assumption that the addition of acetic acid does not alter the miscibility of the chloroform and water ; in fact, their mutual solubility is increased by acetic acid, so that the constancy of the values of K_1 shown in the last column is of fictitious value. Bancroft points out that the agreement of results with a formula does not always prove that the premises on which the formula is based are correct.

Freezing-point Method. Nernst investigated a similar case, the distribution of acetic acid between benzene and water, by means of the freezing-point. In one experiment, using the Beckmann freezing-point apparatus, 5·075 grams of water and 31·5 grams of benzene were placed in the tube. The freezing-point was found to be 5·9° (only the benzene layer freezing), and this, owing to the very slight solubility of water in benzene, is practically the freezing-point of pure benzene. Small weighed quantities of acetic acid were then added. The acid distributed itself between the two solvents, and when the freezing-point (that of the benzene solution) was determined, this was lowered by the acetic acid dissolved in it. To find the concentration corresponding to a given lowering of the freezing-point of the benzene solution, a separate series of experiments was carried out in which weighed quantities of acetic acid were added to a weighed amount of benzene, no water being present. From the curve so obtained the concentration of the acid in benzene corresponding to a given lowering could be determined ; then, knowing the total amount of acid and benzene present, the amount of acid in the water layer can be obtained.

Results. Calling C_1 the number of grams of acetic acid in 5·07 grams of water, and C_2 the number of grams of acetic acid in 31·5 grams of benzene, the following results were obtained :

$t°$ C.	C_2	C_1	$\frac{C_1}{C_2}$	$\frac{C_1^2}{C_2}$
0·075	0·043	0·245	5·7	1·40
0·120	0·071	0·314	4·4	1·39
0·158	0·094	0·375	4·0	1·49
0·240	0·149	0·500	3·4	1·67

Distribution of a Base between Two Acids. Dawson and Grant used the partition method to determine the ratio of the distribution of a base between two acids. If the solution contains the two acids HA and HB and the base MOH, neglecting dissociation we shall have present the four substances HA, HB, MA, MB, if there is insufficient base to neutralize both the acids. If now the solution is shaken up with an immiscible solvent capable of taking up only one of these four substances, say HA, we can determine the proportions of the four substances if we know the amounts of the two acids, and the base used. It was found that while acetic acid was taken up by chloroform, tartaric, malic, citric, and succinic acids were not. Take the case of the distribution of caustic soda between acetic acid and tartaric acid. The first step was to determine the distribution of acetic acid between chloroform and water: the method used has been described in the previous section. A diagram was then plotted showing the relation between the concentration of the chloroform, C_2, and the ratio C_1/C_2. From this curve, the value of C_1, corresponding to an experimental value of C_2, can be worked out. The influence of sodium acetate and tartaric acid on the distribution of the acetic acid between the water and chloroform was tested experimentally and found to be so small as to be negligible. Normal solutions of acetic acid, tartaric acid, and caustic soda were then prepared. Equal quantities of the three solutions were mixed, using a small excess of acetic acid to compensate for that taken up by the chloroform, and the mixture diluted to the required volume; for example, in one experiment 20 ml. of N tartaric acid, 20 ml. of N sodium hydroxide, and 20·7 ml. of N acetic acid were mixed and diluted to 100 ml. 60 ml. of this solution were shaken with 60 ml. of chloroform. On titration the aqueous layer was found to contain 0·1990 gram equivalents per litre of acid and the chloroform layer 0·005632.

The original N tartaric acid was diluted to 0·2 N in making up the mixture.

The original N sodium hydroxide solution was diluted to 0·2 N in making up the mixture.

The acetic acid therefore from the titration is 0·199 N.

From the curve the distribution ratio when the chloroform solution contains 0·005632 is found to be 28·3, hence the free acetic acid in the aqueous solution is $0·005632 \times 28·3, = 0·1593$. The sodium acetate must then be $0·199 - 0·1593 = 0·0397$. This leaves $0·2 - 0·0397$ of 'caustic soda' to combine with tartaric acid, hence the sodium tartrate is 0·1603 gram equivalents per litre and so the uncombined tartaric acid will be $0·2 - 0·1603 = 0·0397$. The ratio of sodium tartrate to sodium acetate is therefore

$$\frac{0·1603}{0·0397} = 4·04$$

The Hydrolysis of Salts. Such a measurement has also been made by means of distribution experiments by Farmer. Suppose a gram-molecule of aniline hydrochloride is dissolved in V litres of water. If the degree of hydrolysis is x, the concentration of free aniline and free hydrochloric acid will be x/V gram-molecules per litre. If the distribution ratio of aniline between benzene and water is first determined and then the aniline hydrochloride solution is shaken with benzene and the aniline concentration in the latter is determined, from the distribution ratio of the concentration of the free aniline the amount of water is obtainable, and then, knowing the amount of aniline hydrochloride originally present, the degree of hydrolysis can be calculated. In one experiment 1 litre of water, containing 0·09969 gram-molecule of aniline hydrochloride, was shaken with 60 ml. of benzene at 25°. The benzene layer was found to contain 0·001156 gram of aniline per ml.; 59 ml. of benzene therefore contained $\frac{59 \times 0{\cdot}001156}{93}$ gram-molecules of aniline = 0·000733; 59 ml. is used in the calculation instead of 60 ml., to allow for the solubility of benzene in water. The water therefore contains 0·09969 − 0·000733 = 0·098956 gram-molecule of free and combined aniline. The partition coefficient being 10·1 (benzene/water) the molecular concentration of free aniline in the water layer is $\frac{1{\cdot}156}{93 \times 10{\cdot}1} = 0{\cdot}001232$, and the amount of combined aniline must therefore be 0·098957 − 0·001232 = 0·097725 gram-molecule. This will also be the amount of combined acid, leaving 0·09969 − 0·09773 = 0·00196 of free acid.

x being the fraction hydrolysed, we have:

$$\frac{x^2}{(1-x)V_m} = \text{const.} = \frac{0{\cdot}00123 \times 0{\cdot}00196}{0{\cdot}09773} = 0{\cdot}0000247$$

whence x = 0·0156 or 1·56 per cent.

The first step in the experiment is to determine the distribution of aniline between benzene and water: 1,000 ml. of water and 60 ml. of benzene are used; 1 ml. of benzene is found to go into solution in the water, leaving 59 ml.; 0·2 gram of aniline is then added and the mixture shaken in the thermostat until equilibrium is attained; 50 ml. of the benzene layer after filtration are removed and the aniline hydrochloride is precipitated by means of a current of dry HCl gas, the benzene evaporated off and the aniline hydrochloride weighed. The experiment is then repeated, using 0·1 gram of aniline. The total weight of aniline used is known, the weight in the benzene layer can be calculated, and so by difference that in the water layer.

Further Applications. Other practical applications of the distribution law are Dawson and McRae's work on metal ammonium compounds by the distribution of ammonia between aqueous solution and chloroform; the extraction of alkaloids by shaking aqueous solutions with chloroform, e.g. Siedell found that 0·125 gram of strychnine shaken with a mixture of equal volumes of water and chloroform distributed itself in the ratio of 0·002 to 0·123, so that the alkaloid in an aqueous solution can be removed practically completely by shaking three times with an equal volume of chloroform. Another example is the determination of the higher alcohols in spirits. The distillate containing ethyl alcohol and the higher alcohols is brought to a specific gravity of 1·1 by the addition of a saturated sodium chloride solution and is then shaken successively with 40, 30, 20, and 10 ml. of carbon tetrachloride, in which the higher alcohols are soluble but not the lower.

CHAPTER VIII [3]

OSMOTIC PRESSURE

SECTION 1: MEASUREMENT

WHEN a solid is dissolved in a liquid the molecules of the dissolved substance can move about in the solvent. The distances between the dissolved molecules, especially in dilute solution, are generally very large in comparison with the diameters of the molecules of the solute or solvent. To some extent this is an analogous state to that found in a gas except that in the latter case the space between the gas molecules is empty, while in the solution there are the molecules of the solvent surrounding the solute molecules.

Van 't Hoff was one of the first to note the analogy between such a system and that existing in a gas. If a small open vessel containing a salt solution (e.g. copper sulphate in water) is placed at the bottom of a large trough filled with water, the copper sulphate slowly diffuses through the entire mass until it is evenly distributed. Again, if two miscible solutions of different gravities are placed in a beaker—the denser at the bottom—and allowed to stand, it will be found after some time that the entire mass will be of similar composition.

Fick's Diffusion Coefficient. If a cylinder contains a salt solution of varying concentration falling uniformly with the height of liquid, and if A is the cross-section of the cylinder, C the concentration of the solute at a given level and $C-dc$ the concentration at a level dl cm. higher and dS is the amount of solvent passing in the time $d\theta$ across the area A, then the following relationship holds:

$$dS = -DA\frac{dC}{dl}.d\theta$$

The diffusion coefficient represents the number of grams of solute crossing 1 sq. cm. in 1 second for a concentration gradient of 1 gram per cm. D is approximately constant. The rapidly diffusive substances were found by Graham to be generally substances that were acids and substances that were crystalline in the solid state. Gum, starch, albumen, glue, &c., diffused very slowly. He distinguished these two groups by calling the former crystalloids and the latter colloids. Graham formulated the theory that the dissolved substance exerted some form of pressure analogous to that of a gas under related conditions with the solvent eliminated. To distinguish between the two types, this pressure in the latter case is called *osmotic pressure*. Assume we have a membrane through which the solvent can pass freely but not the solute. Such a membrane could be utilized as a partition to separate solvent and solution. A simple apparatus to show the phenomenon of osmosis in a qualitative way could be devised as follows: A membrane of parchment is placed on the mouth of a small glass funnel and a solution placed in the inverted funnel which is suspended in a vessel of distilled water. Water passes slowly through the membrane into the solution. The pressure exerted to cause this transfer represents the osmotic pressure. The membrane in the above example allows the free passage of the solvent but stops the passage of the dissolved substance. In contrast to this phenomenon there are other membranes that act differently. They allow solvent and electrolyte to pass through certain membranes but prevent the passage of colloidal particles. This latter phenomenon is quite distinct from that of osmosis and is known as *dialysis*. It is important in the study of colloids and is considered as a separate topic in that chapter later.

For the quantitative measurement of osmotic pressure it is important to obtain the proper type of membrane and various ways of measurement will be reviewed.

The first accurate determinations of the osmotic pressure of solutions were carried out by Pfeffer, who found that a membrane of copper ferrocyanide precipitated in the walls of a porous earthenware pot could withstand the considerable pressures generated in the necessary experiments. Previously Traube had observed that such membranes were permeable to water or other liquids, but not to many dissolved substances. Such membranes are known as semi-permeable membranes and must always be employed in all determinations of osmotic pressure.

Preparation of Semi-Permeable Membranes. The air is removed from the walls of a porous cell by boiling it in water under reduced pressure and the cell is placed in a 3 per cent solution of copper sulphate until the walls are thoroughly impregnated with the salt. It is then washed with distilled water, filled with a 3 per cent solution of potassium ferrocyanide, and reimmersed in the solution of copper sulphate. A precipitate of copper ferrocyanide is formed in the pores of the cell near the inner surface. The cell is then thoroughly washed.

Adie's Modification of Pfeffer's Method (Fig. 1 (VIII^3)). The porous cell *a* is fitted with a glass tube *b*, the jointing being effected by means of sealing-wax; the tube is shown before connecting to a manometer, which contains mercury from *d* to *c* and air above this. A solution the osmotic pressure of which is being determined is poured into the cell through *e* until the remainder of the apparatus is completely filled. *e* is sealed and the cell is then immersed in

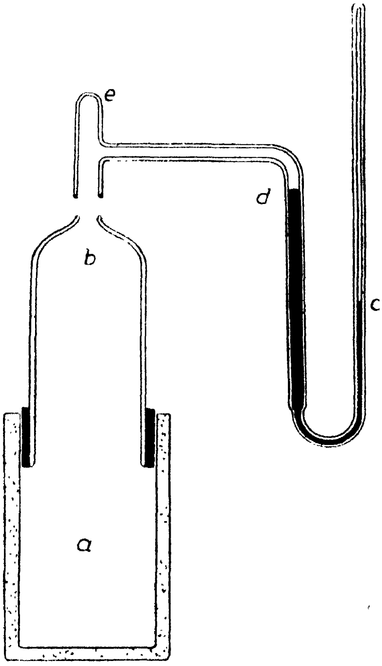

FIG. 1 (VIII^3)
Adie's osmotic pressure apparatus

pure water. The whole apparatus is immersed in a thermostat. The water enters slowly and the pressure increases to a constant value after days or weeks. The amount of water which enters is so small that the dilution is not important, but where necessary it may be estimated by the diminution in the volume of the air.

That the final pressure so obtained is equivalent to the osmotic pressure, that is to the excess of pressure on the solution side of the membrane, can be deduced from theoretical considerations.

Laws of Osmotic Pressure. Quantitative experiments with dilute cane-sugar solutions of varying solution concentrations and at different temperatures show that for dilute solutions the osmotic pressure is directly proportional to the concentration and approximately to the absolute temperature. The laws of osmotic pressure are, as pointed out by van 't Hoff, similar to those relating to gaseous pressure. In other words, the osmotic pressure of a substance in dilute solution is equal to the pressure which it would exert as a gas at the same temperature and occupying the same volume as the solution of it could exist as a gas under such conditions. This is especially true of dilute (about 1 per cent) solutions.

Calculation of Molecular Weight. Hence, if P is the osmotic pressure of a solution at absolute temperature T, which contains 1 gram-molecule of dissolved substance in volume V, then PV = RT, where R is the absolute constant corresponding to 1 gram-molecule of any perfect gas. It is probably more correct to take V as the volume of the solvent rather than that of the solution.

If m grams of a substance of molecular weight M be dissolved in n grams of a solvent, and if the resulting solution has a density d at T° absolute, the volume of solution $= \frac{m+n}{d}$ ml.

If the osmotic pressure of the solution is P mm. of mercury at T° absolute, then the osmotic pressure at 0° is $= \frac{273\text{P}}{\text{T}}$ mm. And the osmotic pressure, if the volume of the solution is 22·41 litres,

$$= \frac{273\text{P}}{\text{T}} \cdot \frac{\frac{m+n}{d}}{22{,}410}\text{ mm.} = \frac{273\text{P}}{\text{T}} \cdot \frac{\text{V}}{22{,}410}\text{ mm.}$$

if V is the volume of the solution in ml. at T° absolute. Hence, since m grams exert this pressure in 22·41 litres at 0°,

$$760\frac{22{,}410 . \text{T} . d . m}{273\text{P}(m+n)}\text{ grams}$$

would exert a pressure of 760 mm. in 22·41 litres at 0°.

$$\therefore \text{M} = \frac{760 \times 22{,}410 \times \text{T} \times d \times m}{273 \times \text{P} \times (m+n)}$$

$$= \frac{62{,}390 \times \text{T} \times d \times m}{\text{P} \times (m+n)}$$

$$= \frac{62{,}390 \times \text{T} \times m}{\text{P} \times \text{V}}$$

If P is expressed in atmospheres

$$M = \frac{82{\cdot}09 \times T \times d \times m}{P \times (m + n)} = \frac{82{\cdot}09 \times T \times m}{P \times V}$$

Conversely, the osmotic pressure of dilute solutions can be calculated approximately if the molecular weight of the solute in the solution be known.

Anomalous Results. If the solute under observation dissociates in solution into ions, abnormal values for the osmotic pressure are obtained. It appears that each ion produces its own specific effect as if it were a complete molecule. Conversely, if the substance is associated in solution, values lower than those expected are obtained for the osmotic pressure. Similar effects are observed in connexion with the lowering of solvent vapour pressure and the other phenomena related to osmotic pressure.

Owing to the difficulty of obtaining accurate results, and to the length of time required for the maximum osmotic pressure to be attained, osmotic-pressure determinations are very seldom employed to measure molecular weights.

Example. Pfeffer found that the osmotic pressure of a 1 per cent aqueous solution of cane-sugar is 493 mm. at 0°.

Here $d = 0{\cdot}996$, $n = 100$, $m = 1$, $T = 273$, $P = 493$

$$M = \frac{62{,}390 \times 273 \times 0{\cdot}996 \times 1}{493 \times 10} = 341$$

Van 't Hoff for a 1 per cent solution takes 1 gram of sugar and 100 grams of water and obtains a volume of 100·6 ml.

Other Semi-permeable Membranes. Other substances which may be employed as semi-permeable membranes include ferric hydroxide, gelatine tannate, calcium phosphate, Prussian blue and silicic acid. A large number of such membranes also occur naturally in plant and animal cells.

Isotonic Solutions. Solutions having the same osmotic pressure as each other are termed *isosmotic* or *isotonic.* Tammann describes an optical method of determining whether solutions are isotonic or not. A drop of potassium ferrocyanide at the end of a capillary pipette is immersed in copper sulphate solution, when a membrane of copper ferrocyanide is at once formed. According as the osmotic pressure inside is greater or less than outside, water enters or escapes and the cell expands or contracts. At the same time striae can be observed in the copper sulphate solution around the membrane owing to the changes in concentration produced. If water enters the cell an increase in concentration occurs and the striae descend. If water leaves the cell, a decrease takes place and they rise ; with isotonic solutions none are visible. Other substances may be dissolved in either or both solutions before the cell is formed, and a variety of determinations carried out in this way.

Osmotic Pressures of Concentrated Solutions. Berkeley and Hartley have examined the osmotic pressures of concentrated solutions, using membranes of copper ferrocyanide capable of withstanding pressures exceeding 100 atm. Equations of the van der Waals type were found to give a good representation of the results with cane-sugar solutions containing 850–180 grams per litre, but since the values of the critical point derived from such equations are impossible, they can only be regarded as applicable in special cases. The calculation is generally not justifiable, since the value of the constant in van der Waals' equation is known to vary with the temperature.

Fig. 2 (VIII[3]) shows the apparatus devised by Frazer and Myrick.[1] It consists of a porous clay cup with a membrane of copper ferrocyanide (K) deposited on its exterior. The solvent and not the solute can pass through this membrane. J is a bronze cylinder into which the cell is fastened by means of the plug P. R is a glass U-tube, held in the mouth of the cell by means of the rubber stopper Q. I is a solution to be measured. A is a piece of capillary tubing to which the manometer is sealed. In this apparatus pressures as high as 270 atm. can be measured. An equilibrium is reached in a few hours so that measurements are completed in a day.

In the Lotz and Frazer modification [2] an improved manometer is employed. This consists of a water interferometer. This osmotic apparatus is claimed to be quicker in action and more dependable. High pressure can also be measured.

Osmometers for Solutes of High Molecular Weight. Owing to the very small osmotic pressure of such solutions, the experimental technique must be very accurate to obtain even approximate values. Again such solutions from high polymers deviate widely from ideal behaviour in the sense that when the value of the osmotic pressure is plotted against the concentration a line bending upwards from the concentration axis is obtained instead of a line parallel to it as in an ideal solution. It is therefore necessary to conduct an extrapolation to infinite dilution.[3]

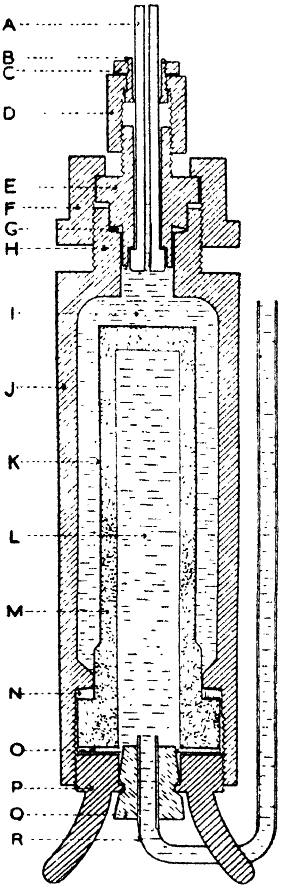

FIG. 2 (VIII[3])
Osmotic pressure apparatus for concentrated solutions

Osmotic Pressure of Egg Albumin Solution. The values of the molecular weight of egg albumin have been determined by various workers using different methods. The molecular weight is of the order of 40,000. These values have been collected by Bull,[4] and are shown in the table appearing on the next page.

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[1] *J. Amer. Chem. Soc.*, 1916, *38*, 1907. *Cf.* also Frazer and Lotz, *Ibid.*, 1921, *43*, 2501.

[2] *Ibid.*, 1921, *43*, 2506.

[3] Melville, *Trans. Faraday Soc.*, 1944, *40*, 218.

[4] *J. Biol. Chem.*, 1941, *137*, 143; see also Bull, *Physical Biochemistry*, J. Wiley & Sons, N.Y., 1943.

Method	Mol. wt.	Workers	Bibliographic reference no.
Osmotic pressure	34,000	Sørenson	1
Chemical analysis	33,800	Cohn, Hendry, Prentiss	2
Ultracentrifuge (equilibrium) . .	34,500	Svedberg and Nichols	3
Recalculation of Sørensen's data .	43,000	Adair	4
Osmotic pressure	43,000	Marrack and Hewitt	5
,, ,, (1 determination) .	36,000	Burk and Greenberg	6
,, ,, ...	46,000	Taylor, Adair, Adair	7
Chemical analysis	35,700	Bergmann and Niemann	8
Ultracentrifuge (equilibrium) . .	40,500	Svedberg and Pedersen	9
,, (sedimentation) . .	44,000	Svedberg and Pedersen	9*
Chemical analysis	36,800	Bernhart	11
Osmotic pressure	45,160	Bull	12

* If the diffusion constant of Polson (10) is used, a molecular weight of 44,500 is obtained.

1. *Comp-rend. trav. Lab. Carlsberg*, 1917, *12*, 22.
2. *J. Biol. Chem.*, 1925, *63*, 721.
3. *J. Amer. Chem. Soc.*, 1926, *48*, 3081.
4. *Ibid.*, 1927, *49*, 2524.
5. *Biochem. J.*, 1929, *23*, 1079.
6. *J. Biol. Chem.*, 1930, *87*, 197.
7. *J. Hyg.*, 1932, *32*, 340.
8. *J. Biol. Chem.*, 1937, *118*, 301.
9. *The Ultracentrifuge*, N. York, 1940.
10. *Kolloid Z.*, 1939, *87*, 149.
11. *J. Biol. Chem.*, 1940, *132*, 189.
12. *Ibid.*, 1941, *137*, 143.

It will be seen that there is lack of agreement between these results. Bull has attempted to eliminate some of the uncertainty regarding this determination using a new and simple osmotic pressure apparatus [1] and the values given in the last item in the table represent his value for the molecular weight of the anhydrous substance. The molecular weight of the hydrated albumin he found to be 61,440.

The diagram from Bull's paper [2] is self-explanatory. See Fig. 3 (VIII[3]). It is made of Pyrex. The capillary tube was 0·2 mm. in diameter. The collodion sac which contains the buffered protein solution is attached to the indicated glass tube by first coating the glass tube with stop-cock grease and then slipping the sac over the end of the tube and winding tightly with rubber bands. The 2-hole rubber stopper, with the collodion sac filled with buffered protein solution (about 20 ml. are required for each experiment) in place, is coated with stop-cock grease and inserted into the larger tube which is completely filled with buffer. The rubber stopper is held in place by means of a metal clamp (not shown in figure). Toluene is added from the top of the capillary and forced down the capillary with a gentle air pressure. Small, 1-hole, rubber stoppers are placed in the tubes containing the buffer solution and the protein solution. Their purpose is to decrease evaporation during the experiment.

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[1] See also Oakley, *T. Faraday Soc.*, 1936, *31*, 136.

[2] *J. Biol. Chem.*, 1941, *137*, 145.

The whole apparatus is clamped in a fixed position in a constant temperature-bath at 25°. The stop-cock is allowed to remain open and the levels of the menisci of the buffer solution, of the protein solution, and of the toluene observed with a cathetometer. The stop-cock is then closed. The toluene meniscus immediately begins to drop as buffer solution flows into the collodion sac. Equilibrium is usually attained within 2 hours, although observations are continued for several hours thereafter to be certain that equilibrium has been reached (usually overnight). At the end of the experiment the stop-cock is opened and the initial levels of the buffer solution, of the protein solution, and of the toluene are checked. The difference in the level between the protein solution and the buffer solution is converted into centimetres of water. Likewise the difference in the level between the initial and equilibrium positions of the toluene meniscus is converted into centimetres of water. The osmotic pressure is calculated as the sum of these two pressures.[1]

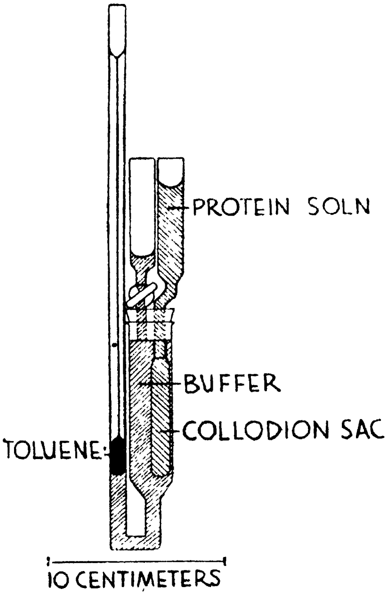

FIG. 3 (VIII^3)
Osmotic pressure apparatus for proteins

The Van 't Hoff formula $\pi/C = RT/M$ accurate for small molecules has been shown to be valid for solutions of high polymers. The absolute molecular weight of the solute— as dispersed in the solvent employed—may thus be calculated.[2]

Osmometer. A simple type of instrument known as the Cenco-Troxel apparatus[3] is available for the visible demonstration of rise of liquid due to osmosis. The features of the osmometer are as follows: (1) Any kind of membrane (cellophane, animal or vegetable parchment, goldbeaters' skin, &c.) may be employed. One of the best membranes according to the manufacturers of the instrument is cellophane. (2) Membranes are easily interchangeable. (3) The solution chamber is easy to fill. (4) No special support is needed; the solution chamber is made of brass, and supporting feet are an integral part of the housing. (5) The relative area of membrane and cross-section of the manometer tube is so great that the rise of liquid is very rapid—several millimetres in a minute. (6) The membrane area is measurable, so that the rate of osmosis can be computed (e.g. ml./cm.^{2}/min.).

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[1] Osmotic pressures have also been measured by Pauli and Fent, *Kolloid Z.*, 1934, *67*, 288, and Bourdillon, *J. Biol. Chem.*, 1939, *127*, 617.

[2] Gee, *ibid.*, 1944, *40*, 260.

[3] Manufactured by the Central Scientific Co., Chicago, Ill.

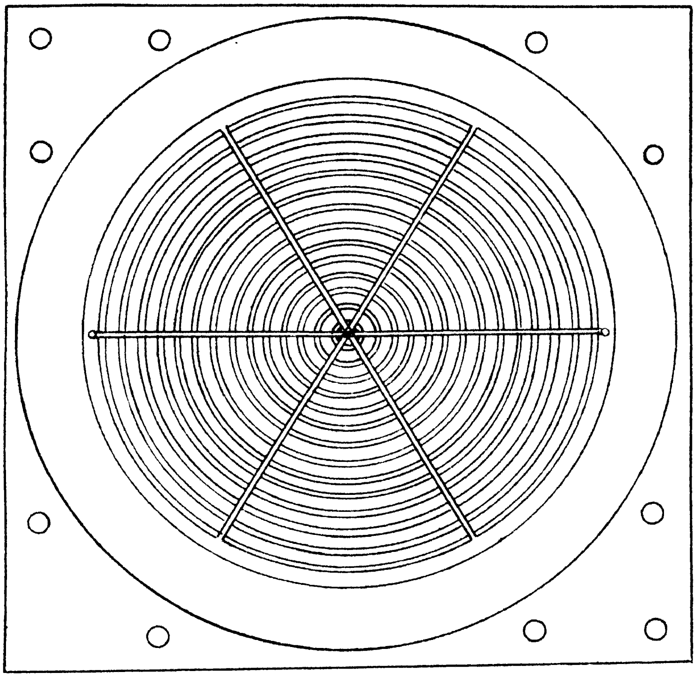

FIG. 4 (VIII[3])
Two brass pieces similar to figure constitute the cell

Osmotic Pressure of Solutions of Cellulose Derivatives. Berkeley and Hartley's method [1] of balancing the osmotic pressure against an artificial pressure has been used by Montonna and Jilk to measure the osmotic pressure of solutions of cellulose derivatives in acetone.[2] The cell used consisted of two similar pieces of half-hardened brass, 14 cm. square and 1·2 cm. thick, Fig. 4 (VIII[3]) each of which was provided with fifteen concentric circular grooves 2 mm. deep, and spaced so that the ridges between them were 1 mm. wide. The grooves were connected as shown in Fig. 5 (VIII[3]), and were 2 cm. wide except for the outermost which was 3 cm. wide and from this there issued through the brass a pair of soldered copper tubes of internal diameter 2 mm.; these tubes are placed diagonally across the plates. Surrounding the outer groove was a ridge 13 mm. wide, machined so that it was exactly the same height as the ridges between the grooves and so that the two outer

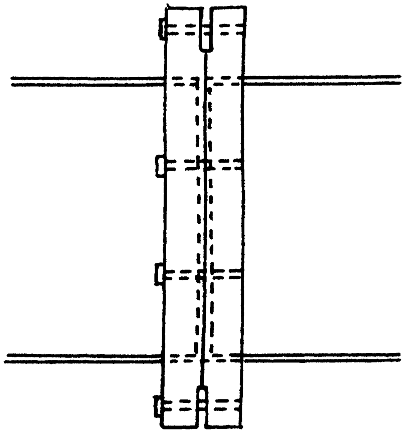

FIG. 5 (VIII[3])
The cell in Montonna and Jilk's apparatus

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[1] *Phil. Trans., A.*, 1906, *206*, 481; 1908, *209*, 319; *Proc. Roy. Soc., A.*, 1909, *82*, 217.

[2] *J. Phys. Chem.*, 1941, *45*, 1374.

ridges when placed together made perfect contact. In closing the cell, a membrane 12·5 cm. in diameter was laid on one half of the cell and the other half was then laid on top, two guide posts ensuring that it was laid in the correct position. Eight cap screws were used to fasten the two halves together so as to make a liquid-tight joint, the membrane itself acting as a gasket. This form of cell gives very good mechanical support to the membrane. Its volume, including that of the lead-in tubes, is about 15 ml.

Preparation of the Membrane

Cellophane and rubber membranes were found to be unsatisfactory and finally one was prepared from collodion which was afterwards denitrated with ammonium sulphide. Merck's C.P. collodion was the only one found to be suitable. The bottom of a wide-mouthed bottle was cut off and the bottle placed mouth downwards on a tripod stand. In it was placed a desiccator plate and on this a large flat dish filled to a depth of 1 cm. with pure clean mercury. A round iron ring 14 cm. in diameter made from a piece of half-inch band iron was floated on the mercury. The bottle was covered with a piece of board with a number of small holes in it. Three inches above the board, a small fan driven at 200–400 R.P.M. created an air current through the bottle to increase the rate of evaporation of the solvent. To prepare the membrane 45 c.c. of Merck's C.P. collodion was run on to the mercury surface inside the iron ring, the pipette tip being half an inch above the mercury surface. The cover was placed on and the fan run for 2 hours. The membrane was then removed from the mercury with the iron ring to which it was firmly fastened. The ring was submerged in distilled water till the membrane broke loose. The edge was trimmed and the membrane denitrated by soaking for 2 hours in a solution consisting of 900 ml. of 5 N ammonium hydroxide saturated with hydrogen sulphide and 100 ml. alcohol. This membrane was then washed in turn with water, carbon disulphide, and acetone and was ready for use after drying for a few minutes in air. Membranes may be stored under distilled water if a desiccator plate is placed on them to keep them flat. Occasionally a membrane was found to be unsatisfactory for no obvious reason. A new membrane was used for each measurement.

Measurements. The apparatus used is shown diagrammatically in Fig. 6 (VIII^3). The vertical distance between each of the overflows on the left was approximately 10 cm. A slow stream of acetone ensured that the level in each section always remained at the overflow and the pressure applied could then be varied by steps by turning on the taps from 1 to 6. In making a measurement of the osmotic pressure of cellulose nitrate in acetone the procedure was to open taps 9 and 10 and introduce 15 ml. of solution into the left side of the cells, the air escaping through tap 10. At the same time taps 6, 7, and 11 were opened to fill the right side of the cell with acetone, air escaping from 11. Tap 12 was next opened to fill the rest of the apparatus with acetone, air bubbles being removed by opening 13 for a few seconds. All taps except 8 and 12 were then closed. The meniscus in the graduated capillary was next brought to the zero position by opening tap 14 for a few seconds. By opening one of the taps 1 to 6, the least pressure can be found which causes the meniscus in the capillary to move to the left, i.e. acetone to pass from solution to solvent: the velocity of the meniscus is determined with a stop-watch for this pressure and for a few higher pressures. The velocities are then plotted against the pressures in cm. of acetone and the straight line so obtained is produced to cut the pressure axis in order to obtain the hydrostatic pressure which prevents any flow through the membrane; this is the osmotic pressure. When the osmotic pressure is so high that a flow from the solution only occurs when taps 5 or 6 are open, some negative rates when the flow is in the opposite direction may be taken and plotted. The apparatus was set up in the air and protected from draughts.

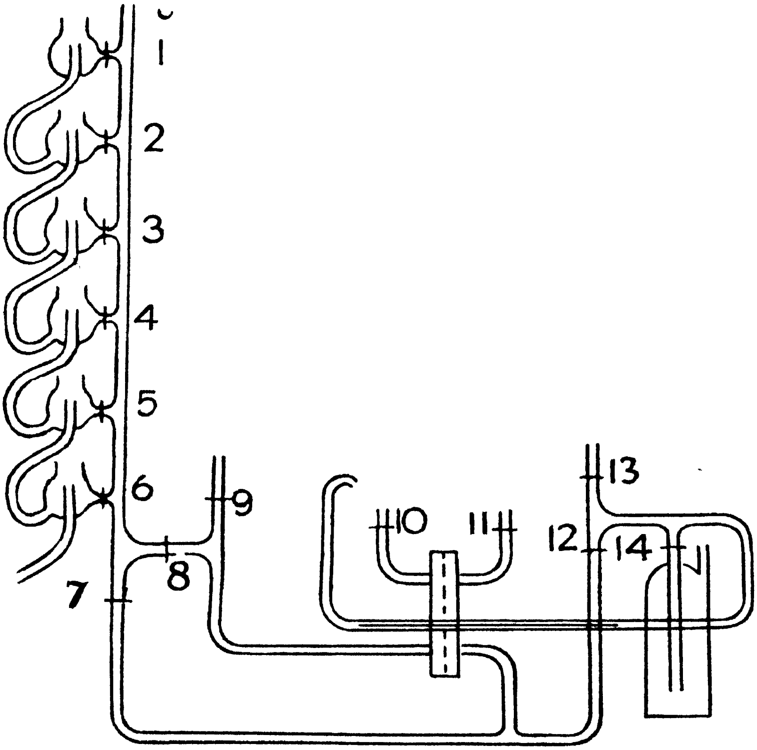

FIG. 6 (VIII[3])
The arrangement of the osmotic pressure apparatus

Carter and Record[1] describe an osmometer working on the counter-pressure principle of Berkeley and Hartley, in which the osmotic pressure is applied externally. A flat ‘ Viscacelle ’ membrane is compressed between the two ground ends of the two glass bulbs of the apparatus and is supported on a slightly convex perforated brass upper plate to prevent movement under changing pressures.

Dry ‘ Viscacelle ’ or ‘ Cellophane ’ (the non-moisture proof variety) swells up in water to a definite maximum and then becomes permeable to water and ordinary solutions. Alcohol exerts little or no swelling effect. Consequently any degree of swelling between these limits may be obtained by immersing the dried membrane in the appropriate alcohol-water mixture. After swelling the membrane is transferred to absolute alcohol and then may be used with any miscible organic liquid without altering the swelling or permeability.

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[1] *J. Chem. Soc.*, 1939, *155*, 660.

Electrical Osmosis involves the measurement of the velocity of flow of a liquid with respect to a solid phase (see Vol. II, Chap. V). For use of ultra-microscope to measure velocity of particles in solution see also Vol. II.

The Dorn Effect[1] (Sedimentation Potential Method). Electro-osmosis is concerned with the movement of a liquid relative to a solid under the influence of an external electric field applied tangentially to the interface. The Dorn effect involves the movement of a solid phase in respect to a liquid under the influence of a mechanical force (e.g. gravity). For further details see Bull[2] as well as Quist and Washburn.[3] These latter workers have developed a technique for this measurement.

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[1] *Anz. Akad. Wiss. Krakau*, 1905, *131*; 1914, *95*.

[2] *Physical Biochemistry*, J. Wiley, N.Y., 1943.

[3] *J. Amer. Chem. Soc.*, 1940, *62*, 3169.

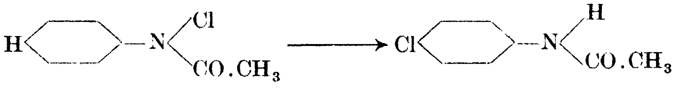
CHAPTER IX[3]

KINETICS OF HOMOGENEOUS REACTIONS

SECTION 1: RATES OF REACTION

GULDBERG and Waage stated the law of mass action, namely, that the rate at which a substance reacts is proportional to the active mass of that substance and also that when chemical equilibrium is established it is due to opposing reaction velocities neutralizing each other. By active mass, molecular concentration is meant. Individual cases of the application of the law had been studied at an earlier date, notably the case of the inversion of cane-sugar by Wilhelmy in 1850, in which he correctly applied the law of mass action and first used the differential equation to get the velocity constant.

Examples. The simplest possible case is that in which one molecular species only undergoes change. An example of such a change is the conversion of acetochloranilide into the isomeric *p*-chloro-acetanilide.



Calling these substances A and B, if we start with a concentration of a gram-molecules of A per litre, according to Guldberg and Waage's law the rate at which A will be transformed into B will be proportional to a, it will therefore be equal to ka where k is a constant called the velocity constant of the reaction. After a time t a certain quantity x of A will have been transformed into B so that the concentration of A is reduced to $a - x$; at this instant, then, the rate of the reaction is proportional to $a - x$ and is equal to $k(a - x)$, where k has the same value as before. We can therefore write

$$\frac{dx}{dt} = k(a - x)$$

On integration this gives

$$k = \frac{1}{t} \log_e \frac{a}{a - x}$$

$$= \frac{2{\cdot}302}{t} \log_{10} \frac{a}{a - x}$$

Since the instant at which the reaction starts may not be known with certainty, it is often useful to write the equation in the form

$$k = \frac{2{\cdot}302}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2}$$

where x_1 and x_2 are the amounts of A converted in the times t_1 or t_2. Reactions of this kind are called monomolecular. Some examples are the decomposition of arsine and phosphine, e.g.

$$4AsH_3 = 6H_2 + As_4$$

the inversion of cane-sugar into glucose and fructose (under special conditions—in presence of a large excess of water),

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

and the hydrolysis of esters, e.g. ethyl acetate, under similar conditions.

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH$$

Zero Order Reactions. When the reaction takes place on the surface of a catalyst which strongly adsorbs one or other of the reactants, the rate of the reaction may be

$$\frac{dC}{dt} = kC_0 = \text{constant.}$$

In such cases it is assumed that as long as an appreciable amount of the strongly adsorbed reactant is present in the solute, the surface of the catalyst where the reaction occurs is almost saturated with this reactant, which is activated by the adsorption process: the other reactant is adsorbed on the remaining small fraction of the catalyst while the products of the reaction must be assumed not to be strongly adsorbed.

Monomolecular Reaction. In the first example it appears at first sight that 4 molecules are involved in the change, yet it obeys the monomolecular law. This is supposed to be due to the reaction taking place in the stages

$$\begin{aligned}&AsH_3 \longrightarrow As + 3H\\&4As \longrightarrow As_4\\&2H \longrightarrow H_2\end{aligned}$$

The last two reactions are extremely rapid, the first is comparatively slow, so that for all practical purposes the time of the first stage is the time of the whole reaction. In the second and third cases 2 molecules appear to be involved. Here the reaction obeys the monomolecular law because in the concentration employed the active mass of the water remains practically constant. For example, if we take a 10 per cent solution of cane-sugar, we have 10 grams of sugar to 90 grams of water, the molecular weight of the sugar is 342, while that of the water is 18. The relative molecular concentrations are then $\frac{10}{342}$ to $\frac{90}{18}$, i.e. as 1 : 171. Thus, when the sugar undergoes 100 per cent change, the water undergoes a change of about 0·6 per cent.

Bimolecular Reaction. When 2 molecules are actually involved in the change so that the active masses of both are altered, we get a true bimolecular reaction. The saponification of ethyl acetate by means of sodium hydroxide illustrates this case:

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH$$

Suppose the initial molecular concentration of the ester to be *a* gram-molecules per litre and of alkali to be *b*. After a time *t* let *x* molecules of ester have undergone change; the change of x molecules of ester involves the change of the same number of molecules of the alkali. At the time t the molecular concentrations of ester and alkali are $a - x$ and $b - x$ respectively. The rate of reaction is then

$$\frac{dx}{dt} = k(a - x)(b - x)$$

This on integration gives

$$k = \frac{1}{(a - b)t} \log_e \frac{(a - x)b}{(b - x)a}$$

Other examples of second-order reactions are:

(1) The bromination of cinnamic acid—

$$C_6H_5.CH : CH.COOH + Br_2 = C_6H_5.CHBr.CHBr.COOH$$

(2) The action of silver nitrate on ethyl iodide in alcoholic solution—

$$C_2H_5I + AgNO_3 = AgI + C_2H_5NO_3$$

(3) The action of hydriodic acid on hydrogen peroxide—

$$\begin{aligned} 2HI + H_2O_2 &= HIO + H_2O + HI \\ HI + HIO &= I_2 + H_2O \end{aligned}$$

—the former reaction being the slower of the two.

Trimolecular Reaction. By reason of the fact that many complex reactions take place in stages, reactions of a higher order than the second are uncommon. An example of a trimolecular reaction is that studied by Noyes and expressed by the equation

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

Here it was found desirable to add a small amount of the products of the reaction to prevent secondary disturbances. When the three substances are present initially in the same molecular concentration

$$\frac{dx}{dt} = k(a - x)^3$$

and

$$k = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2(a - x)^2}$$

The oxidation of nitric oxide to nitrogen peroxide is a third order reaction and might be expressed:

$$NO + NO + O_2 = 2NO_2$$

The rate is proportional to the oxygen concentration and to the square of the NO concentration. This reaction has been investigated by Wourtzel.[1] A reaction may appear judging by final products to be of the third order, but in most cases the systems are found to react in stages in which one stage takes place at a different rate from another. The slower rate determines the rate of the reaction as a whole. The order of the reaction corresponds with the order of the slow reaction.

These various types of reactions will be considered in more detail in the next three sections.

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[1] *Compt. rend.*, 1930, *170*, 229.

Series Reactions. The above type of reactions in which different rates are involved is sometimes called *Series Reactions* or *Chain Reactions.* Examples of these have been studied by Bredig and Walton [1] and Harned; [2] (catalytic decomposition of hydrogen peroxide), by Linhart [3] (reduction of mercuric chloride by phosphorous acid) and by Kistiakowsky and Lenher [4] (oxidation of acetylene).

Reactions of the fourth and fifth order have been found, but are extremely rare.

Each individual case must be treated according to circumstances, and it is possible therefore to give only a selection of examples to illustrate the way in which the measurements are made.

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[1] *Z. physik. Chem.*, 1904, *47*, 185.

[2] *J. Amer. Chem. Soc.*, 1918, *40*, 1467.

[3] *Ibid.*, 1913, *55*, 354.

[4] *Ibid.*, 1930, *52*, 3785.

SECTION 2: ZERO ORDER REACTIONS

Reduction of Tropaeoline

Formic acid reduces the dye-stuff tropaeoline-O (Resorcin yellow) in the presence of colloidal platinum.

The solutions required are

1. N formic acid (free from chloride)
2. 0·005 M Tropaeoline-O. (1·25 grams per litre)
3. Colloidal platinum 1–2 mg./litre (estimate by addition of hydrochloric acid to precipitate the colloid and collect in a Gooch or sintered glass crucible).

All apparatus must be cleaned with acid dichromate and then water. Carry out a preliminary experiment to find out the volume of the platinum solution which should be added to 100 ml. of a mixture of equal volumes of formic acid and the dye solution to decolorize the dye in about 1 hour. Measure out 50 ml. of formic acid and an equal volume of the tropaeoline solution into a conical flask and the necessary amount of colloidal platinum into a test tube: plug the vessels with cotton-wool and place in the thermostat. In another flask prepare a control mixture of 25 ml. of formic acid, 25 ml. of dyestuff, diluted with a volume of distilled water equal to half the volume of platinum solution used; place in the thermostat; when sufficient time has elapsed for the solutions to acquire the temperature of the bath, add the platinum to the mixed solutions and note the time of mixing. At intervals of 10 minutes remove 20 ml. of the solution and add to the acid in one of the numbered flasks; the acid precipitates the colloid and stops the reaction. Finally add 20 ml. of the control solution to 10 ml. of dilute hydrochloric acid. The amount of dye remaining unchanged in all the solutions is now determined by titrating with titanous sulphate in boiling solution. Commence with the control solution, keep it gently boiling and add the titanous solution in a slow stream of drops until the solution shows a considerable reduction of the orange colour; wait for 30 seconds and complete the titration dropwise until the colour becomes a faint brownish yellow. Read the burette and confirm that the end point has been reached by the addition of a further quantity of the titanous solution. This titration gives the concentration of the dye at the start and the final product gives a colour standard for the end of the titration in each of the numbered flasks. When all the titrations have been completed, the titration values are plotted against the time at which the solution was removed: the resulting curve is a straight line, showing that the rate is independent of the concentration.

SECTION 3: MONOMOLECULAR REACTIONS

(1) The Inversion of Cane-sugar:

$$\underset{\text{cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{laevulose}}{C_6H_{12}O_6}$$

Cane-sugar is dextrorotatory, that is, it rotates the plane of polarization to the right. Dextrose is also dextrorotatory ($[\alpha]^{D}_{20} = + 52{\cdot}5)^\circ$, but laevulose is more strongly laevorotatory ($[\alpha]^{D}_{20} = - 92)^\circ$, so that a mixture of equal quantities of the two reaction products is as a whole laevorotatory. As the change proceeds, therefore, the amount of dextrorotation gradually decreases to zero, and the solution then becomes laevorotatory. The progress of the change can thus be followed by means of the polarimeter. The reaction takes place slowly, but is accelerated by acids, so that in order to complete the experiment within a reasonable time an acid solution is used. 20 grams of pure cane-sugar are dissolved in a 100-ml. flask, a crystal of mercuric iodide is added as a preservative, and the solution is made up to the mark with distilled water. A normal solution of hydrochloric acid is also prepared. When equal quantities of these two are mixed we have a 10 per cent cane-sugar solution in N/2 hydrochloric acid; the solutions are to be mixed immediately before the first reading is taken. Two flasks which have been steamed and dried in the usual manner are taken, and into one 25 ml. of sugar solution, and into the other 25 ml. of the HCl solution, are placed. The stoppers are inserted and the flasks are placed in the thermostat at the required temperature, say 25°. A jacketed polarimeter tube is then taken and filled with water, the water circulation from the thermostat is started, and the constancy of temperature of the water in the tube is determined. The water circulation must be regulated so that the temperature is constant to 0·1°, since velocity constants are very sensitive to temperature; in this particular case it becomes 3·63 times as great for a rise of 10°. The zero reading of the polarimeter can now be made, taking the mean of a number of settings. The tube is next removed and dried, replaced in the polarimeter and allowed to remain there for 10 minutes. The two flasks are then removed from the thermostat, their contents are mixed by passing backwards and forwards from one to the other, and the mixture is placed in the polarimeter tube. The initial readings must then be taken as rapidly as possible. The time is taken, five settings of the polarimeter are made and recorded, and the time again noted. The mean of the five readings is taken as the initial rotation and the mean of the two times is the initial time.

After 10 minutes a similar series of five readings of the polarimeter and of the mean time is taken. Similar series are then taken over periods gradually increasing up to 2 hours. The reaction will not be complete until at least 48 hours have elapsed, when a final series of readings must be made. The zero-point of the instrument is then once more determined to ensure that no change has occurred therein.

If the initial and final readings are denoted by a_0 and a_∞ and the reading at time t is a_t the amount which has changed in the time t is $a_0 - a_t$, and the amount still left unchanged is $a_t - a_\infty$. The total amount of sugar present is proportional to $a_0 - a_\infty$, so that

$$k = \frac{1}{t}\log_e \frac{a_0 - a_\infty}{a_t - a_\infty}$$

$$= \frac{2{\cdot}302}{t}\log_{10}\frac{a_0 - a_\infty}{a_t - a_\infty}$$

Some results of Wilhelmy, using nitric acid as the catalyst at 15°, show the results attainable :

t, minutes	$a_t - a_\infty$	$\log_{10}\frac{a_0 - a_\infty}{a_t - a_\infty}$	k
0	65·45	—	—
45	56·95	0·0605	0·00134
90	47·45	0·1217	0·00135
150	40·70	0·1981	0·00132
210	33·70	0·2880	0·00137
270	26·95	0·3851	0·00142

An investigation has been carried out by Pennycuick [1] in order to clear up the uncertainties as to the order of reaction found by different workers. The chief improvement was in the allowance made for the mutarotational lag, a special polarimeter was used in which readings could be taken at 0°· Using this technique he was able to show a slight (4 per cent) increase in k during inversion, an effect which could be explained by the decrease in water content and the increase in hydrogen-ion activity.

Strength of Acids. The same reaction can be used to determine the relative strengths of acids, since these are proportional to their catalysing powers. All that is necessary is to carry out the experiment as described above, but using different acids, each in N/2 solution in the final mixture used. The ratio of the various velocity constants obtained is then the ratio of the strengths of the acids used as catalysts.

(2) The Decomposition of Arsine :

$$4AsH_3 = As_4 + 6H_2$$

Arsine is extremely poisonous, and the following is intended only as a description of a method ; it is not to be used as a student's experiment. The apparatus is that shown in Fig. 1 (IX³). The reaction vessel A is enclosed in the heating reservoir B, where it is heated to a constant temperature by means of diphenylamine (310°) boiling under the reflux condenser G. The tap D is closed and A is connected to the pump and evacuated ; the arsine is then introduced and the tube E is sealed. A is placed in a vessel containing water at the room temperature, the tap D is opened and by raising or lowering the reservoir the mercury is brought to a marked point in C. The height of the barometer and the heights of the mercury in C and F are read, so that the pressure of the gas in A is known. We then have the pressure of the gas at a known volume and temperature. When decomposition occurs the pressure rises at a fixed volume and temperature in the ratio of 2 to 3 (the volume of the solid As is neglected). Hence, if the initial pressure were P_0, when the reaction is complete the pressure will be $\frac{3P_0}{2}$ and at the time t it will be P_t, hence the change in pressure corresponding to the completed reaction is $\frac{3P_0}{2} - P_0 = \frac{P_0}{2}$. When the pressure is P_t the change in pressure which has yet to be completed is $\frac{3P_0}{2} - P_t$, and this is of course the arsine as yet unchanged.

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[1] *J. Amer. Chem. Soc.*, 1926, *48*, 6.

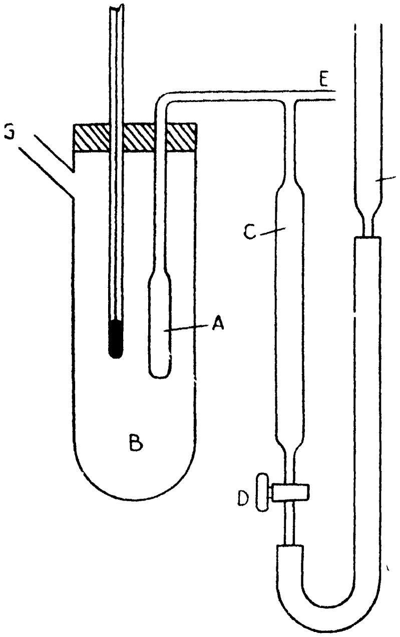

FIG. 1 (IX³)
Apparatus for the determination of arsine

Hence

$$\frac{dx}{dt} = k\left(\frac{3P_0}{2} - P_t\right)$$

$$k = \frac{1}{t}\log_e \frac{\frac{P_0}{2}}{\frac{3P_0}{2} - P_t} = \frac{1}{t}\log_e \frac{P_0}{3P_0 - 2P_t}$$

Therefore after the initial readings have been made A is dried and placed in the diphenylamine vapour for 2 or 3 hours; it is then removed, cooled, and the new pressure read for the same volume. Proceeding in this way the following results were obtained at 310°:

Time in hours	Pressure in mm. of Hg	k
0	784·84	—
3	878·5	0·0908
4	904·05	0·0905
5	928·02	0·0908
6	949·28	0·0905
7	969·08	0·0906
8	987·19	0·0906

(3) The Decomposition of Benzene Diazonium Chloride and other Diazonium Salts:

$$C_6H_5.N:NCl + H_2O = C_6H_5OH + N_2 + HCl$$

From the equation it is seen that the volume of the nitrogen set free is proportional to the amount of chloride decomposed. The reaction is carried out in dilute aqueous solution, and it is found that such a solution readily remains super-saturated with nitrogen; it is therefore necessary to stir the reaction mixture throughout the progress of the reaction. This can be done by means of a stirrer working through a mercury seal as shown in Fig. 2 (IX³). S, the stem of the stirrer, passes through the tube *a*, 4 cm. long, which passes through the rubber stopper *e*; *b* is a tube 3 cm. long and 12 mm. external diameter, which passes half-way through the stopper *e*. Mercury is poured between *a* and *b*. On the stem S is fixed by means of rubber tubing a short piece of tube *c*, which bears on the top of *a*, and on *c* is fixed by means of a rubber stopper the tube *d*, which is intermediate in diameter between *a* and *b*, and which dips down into the mercury. A coat of vaseline on S serves to diminish friction. The reaction is carried out in a large test tube (15 cm. by 3 cm.) which has a narrow-bore side-tube at the top for connecting to a Hempel burette. Since the experiment continues for a considerable time the measuring tube of the burette should be surrounded by a water jacket so that its temperature can be kept constant. The solutions must be freshly prepared for each experiment; 6·64 grams of pure aniline are dissolved in 21·5 ml. of hydrochloric acid (specific gravity 1·16), 4·93 grams of sodium nitrite are dissolved in 75 ml. of water. The two solutions are cooled in ice and the nitrite is then slowly added to the aniline solution by means of a dropping funnel, the lower end of which dips below the surface of the aniline solution. The mixture is kept well shaken, and the rate of addition controlled so that the temperature is kept low. The solution so

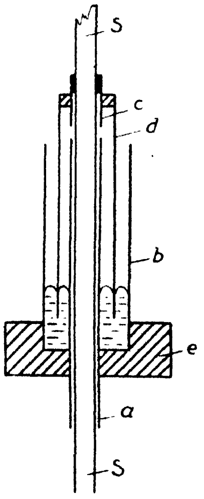

FIG. 2 (IX³)
Stirrer working through a mercury seal

obtained is then made up to 1 litre, giving a solution containing 10 grams of the diazonium chloride per litre. Sufficient of the solution is placed in the test tube to fill it nearly to the level of the side-tube. The stopper and stirrer are inserted and the tube is fixed in the thermostat (25°) and the stirrer is started. After 7 to 10 minutes the side-tube is joined to the burette and this time is taken as the zero time for the experiment. The burette is levelled to atmospheric pressure, the volume and temperature readings are taken and recorded, and also the height of the barometer. The next reading is taken after 2 hours and then at intervals of an hour, the pressure in the burette being adjusted to atmospheric each time, and volume, temperature, and barometric height being recorded. After 8 hours the reaction may be brought to completion so as to obtain the total volume of nitrogen. This is done by removing the tube from the thermostat and placing it in a beaker of hot water for 15 minutes, replacing in the thermostat, and after 10 minutes reading the volume. This process is repeated until the volume remains unaltered, indicating the completion of the reaction. The velocity constant can then be calculated from the volume of nitrogen set free.

Typical results from diazotizing aniline in hydrochloric acid are as follows [61 ml. is the total volume of nitrogen (at 14° and 741 mm.) calculated from the amount of aniline used]:

Time in minutes Solution kept at 20°	Volume of nitrogen in ml. at 14° and 741 mm.	k
451	31·4	0·00159
506	34·4	0·00163
607	40·5	0·00179
1382	55·3	0·00170
∞	61·0	—

The diazonium salts from heterocyclic amines generally show a close resemblance to similar substances from aromatic amines. Many of the heterocyclic diazonium salts, however, even in ring compounds of a simple nature, show a remarkable stability, in marked contrast with corresponding benzenoid substances.

The titration method of Hirsch is generally not satisfactory for the investigation of these substances. The direct application of the physico-chemical method of Hausser and Müller is also to some extent unsatisfactory. A more recent process for the study of the decomposition of diazonium salts consists in heating, in a thermostat, a solution of the diazonium salt contained in a quartz tube, through which a current of air-free carbon dioxide (prepared by Farmer's method [1]) is passing, and collecting the nitrogen evolved over potassium hydroxide solution. The apparatus used by Reilly and Madden [2] is shown in Fig. 3 (IX[3]). A definite volume of a solution containing a known weight of the amine (sufficient to give 56 ml. of gas at *S.T.P.*, normal diazotization being assumed) was heated in a specially constructed quartz vessel, A, fitted with a ground stopper into which was sealed a tube passing to the bottom of the vessel. The vessel was contained in a thermostat, B, at 101·5°, which temperature was found to keep the solution of the diazonium salt at 100°, and was connected through a condenser, C, to a water-jacketed nitrometer, D. A current of air-free carbon dioxide was periodically passed through the solution, and the liberated nitrogen was collected over concentrated aqueous potassium hydroxide. In decomposition at high temperatures a condenser is placed between the tube containing the solution and the water-jacketed azotometer. By the use of the stream of inert gas it is possible to overcome the difficulties met with by earlier investigators. Thus, by means of a control experiment, the time necessary for the solution to acquire the temperature of the thermostat is determined. A thorough sweeping with carbon dioxide expels the nitrogen formed during this time, so that the true starting-point can be determined. Further, no allowances are necessary for the expansion of the solution and air in the apparatus.

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[1] *J. Chem. Soc.*, 1920, *117*, 1446.

[2] *Trans. Chem. Soc.*, 1925, *127*, 2936, and 1929, *134*, 815.

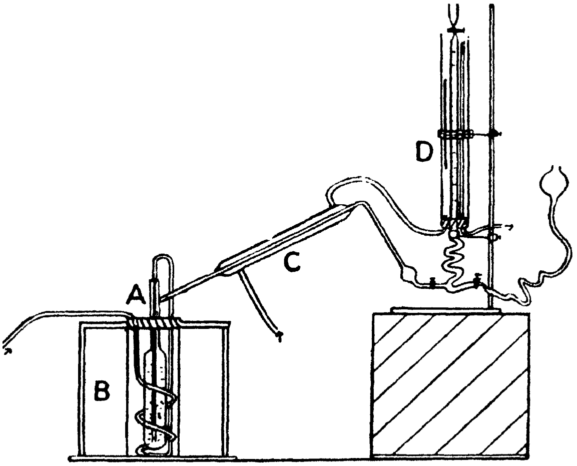

FIG. 3 (IX[3])
Apparatus for decomposition of a diazonium salt and for the collection of evolved nitrogen

As an example of the stability of these compounds under the conditions of the experiment the following figures for the diazonium chloride from 4-amino-1-phenyl-3 : 5 dimethyl-pyrazolone are given. After 5 hours' heating at 100°, approximately 45 per cent of the possible amount of ' diazo ' nitrogen is evolved ; after 10 hours', about 70 per cent, and after 20 hours' less than 90 per cent. At this stage the rate of gas evolution is very small (0·2 ml. per hour), indicating that secondary reactions have taken place. During the main period of the experiment the decomposition of the diazonium chloride followed the course of a unimolecular reaction. The decomposition of the diazonium nitrate closely resembles that of the chloride, but, in the case of the sulphate, however, the reaction is more rapid at the beginning, and the total evolution of gas smaller, showing increased secondary reaction. The anion, in some cases therefore, appears to influence the rate of decomposition, unlike the results with benzenoid diazonium salts.

A modified simple and accurate apparatus for measurement and recording of evolved nitrogen has been designed by Crossley, Kienle and Benbrook.[1] The apparatus is shown in Fig. 4 (IX^3). It has been used, for example, for the study of the decomposition of diazotized aniline. It is equipped with an efficient stirrer to prevent super-saturation of the solution with nitrogen. The volume of the gas evolved from the reaction cell was continuously measured and recorded. One example for the use of the apparatus will be quoted.

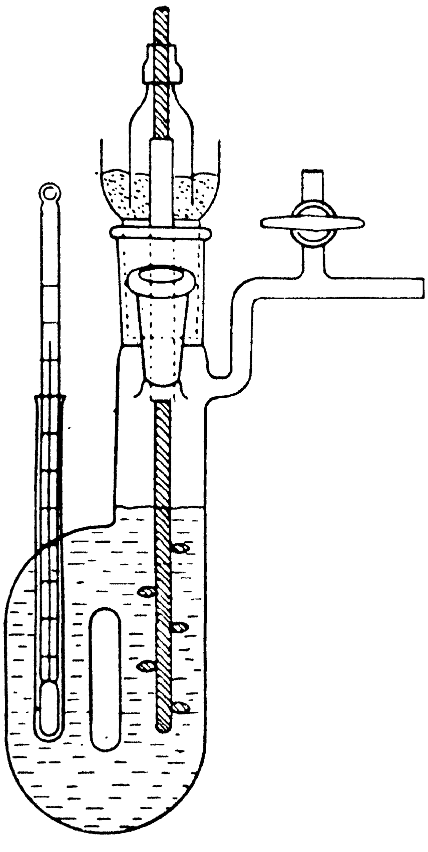

FIG. 4 (IX^3)

Apparatus for the quantitative study of the decomposition of a diazonium salt

Freshly distilled aniline was diazotized at 0–5° in aqueous solution using 2·2 molar equivalents of hydrochloric acid and 1·0 molar equivalent of sodium nitrite. The solution was diluted to 0·1 molar concentration with ice water, immediately added to the reaction cell and brought to the experimental temperature. The rate of decomposition was determined over a wide temperature range.[2] The values of the reaction velocity constants are given in the table.

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[1] *J. Amer. Chem. Soc.*, 1940, *62*, 1400.

[2] *Loc. cit.*

EFFECT OF TEMPERATURE ON THE REACTION VELOCITY OF DECOMPOSITION OF PHENYLDIAZONIUM CHLORIDE SOLUTION OF CONCENTRATION 0·1 MOLAR AND pH 1·6-1·8

Temp., ° C.	$k(\text{sec.}^{-1}) \times 10^6$
5	0·15
25	4·10
35·2	20·0
50	140·0

The data in the table are linear when plotted as lnk *vs.* 1/T, thus satisfying the Arrhenius equation

$$lnk = lnZ - (E/RT)$$

The heat of activation for the reaction has been calculated from these data and found to be 27,200 cal./g. mole.

Formation of Diazonium Salts. The velocity of formation of diazonium salts has also been studied by Reilly and Bastible.[1] The rate of formation of diazonium salts was ascertained by estimating the amounts of nitrous acid present at varying intervals in a reacting mixture of definite amounts of base and sodium nitrite and mineral acid. The quantity of nitrous acid found was a measure of the amounts of the diazonium salts which were formed in certain time intervals, and so was a measure of the rate of the reaction.

Owing to the very rapid formation of diazonium salts in concentrated solutions, very dilute solutions were employed, the reaction being carried out in N/1,000 solutions, and the estimations made in N/100,000 solutions. The effect of this dilution is to retard greatly the rate of the reaction, and so render it capable of more accurate measurement. The method of procedure closely followed that employed by Hantzsch and Schumann for aniline, except that the colorimetric estimation of nitrous acid, instead of being made in ordinary standard Nessler tubes, was carried out in a modified Klett Bio-colorimeter of the Duboscq type. Potassium iodide was used in preference to zinc iodide, as this latter reagent is extremely sensitive, and is influenced by the presence of even traces of impurities. The method of working with the Klett instrument is described in the chapter on Colorimetry. In the improved method of Reilly and Drumm [2] the rates were calculated by direct measurement of the amount of diazonium salt present at various intervals of time: the diazonium solution was coupled with an alkaline solution of Schaeffer's acid, and the solution of the resulting azo-dye was matched in a colorimeter with one similarly and simultaneously prepared from a completely diazotized solution of the amine.

The generally accepted view of the mechanism of diazotization of aromatic amines is that first advanced by Hantzsch and Schümann,[3] according to whom interaction takes place between arylammonium ions ArNH$_3$, resulting from the ionization of the amine salt, and undissociated nitrous acid. It follows that (1) amines of different basicities should, in the absence of excess of mineral acid, diazotize at different rates, the order of which should coincide with the order of the basicities; (2) the rate of diazotization of an amine should not be altered appreciably by the presence of a greater amount of acid than that necessary for the prevention of hydrolysis of the amine salt.

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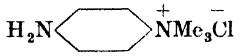
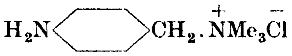
[1] *Sci. Proc. Roy. Dub. Soc.*, 1926, *18*, 28, 343.

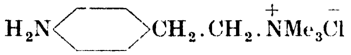
[2] *J. Chem. Soc.*, 1935, *146*, 873.

[3] *Ber.*, 1899, *32*, 1691.

In support of this view Reilly and Drumm carried out the following experiments. Three amines were chosen in which a strongly positive pole $\overset{+}{N}Me_3$ was attached to the nucleus (I) or separated from it by one (II) or two (III) methylene groups. In (I) the positive pole $\overset{+}{N}Me_3$ will induce a drift of the unshared salt-forming electrons of the amino-nitrogen atom in its direction, thereby reducing the tendency of the nitrogen atom to attract positive ions ($\dot{H}$) and so leading to a depression of the basic character of the amino-group. In (II) and still more in (III) the attraction of these electrons by the positive pole will be decreased by the insertion of the neutral methylene group or groups, the result being a strengthening of the basicity of the amino-group. The order of basicity of these amines will be, therefore, (III) > (II) > (I) and, according to the mechanism of Hantzsch and Schümann, the rate of diazotization of (III) should be greatest and that of (I) least.


(I)


(II)


(III)

The results of the following table (column 2) are in agreement with this view, and further support for the Hantzsch-Schümann theory is the fact that the rate of diazotization of any particular amine is practically the same whether two or four molecules excess of hydrochloric acid are present.

Temp. 1°. k = Velocity constant $= 1/t . x/a(a - x)$.

Amine	$RNH_3Cl + HNO_2$ k	$RNH_3Cl + HCl + HNO_2$ k	$RNH_3Cl + 2HCl + HNO_2$ k	$RNH_3Cl + 4HCl + HNO_2$ k
(I) . .	0·012	0·033	0·040	0·041
(II) . .	0·022	0·036	0·038	0·039
(III) . .	0·027	0·038	0·039	0·038

A further conclusion to be drawn from these results is that the ions of the bases, in the presence of excess of mineral acid, are converted at approximately the same rate into diazonium ions.

On account of the very rapid formation of diazonium salts in concentrated solution, the rate of reaction was measured in N/1,000-solution, where it is so retarded as to be capable of more accurate measurement. Further, as the formation of diazonium salt proceeds somewhat irregularly at the commencement, the speed of the reaction is best calculated after a certain interval.

Hantzsch and Schümann[1] measured rates of diazotization indirectly by estimation of the free nitrous acid from time to time with starch-iodide. This method proved unsuitable in the present instance, and the rates were calculated by direct measurement of the amount of diazonium salt present at various intervals of time: the diazonium solution was coupled with an alkaline solution of Schaeffer's acid, and the solution of the resulting azo-dye was matched in a colorimeter with one similarly and simultaneously prepared from a completely diazotized solution of the amine.

In the above work variation is induced in one substituent and is not the same as the case where different substituents are attached to different positions in the benzene ring. Such substituents, according to Boeseken and Schoutissen,[2] have two opposing influences on diazotization. The velocity diminishes with increasing substituents in the order *m*, *p*, *o* on account of decreasing basicity. The effect, however, is counteracted by increase in the velocity of conversion of the amino-group to the quaternary salt, substituents acting in the reverse order to the above.

(4) **The Esterification of Cinnamic Acid in the Presence of Hydrochloric Acid:**

$$C_6H_5.CH:CH.COOH + CH_3OH = C_6H_5.CH:CH.COOCH_3 + H_2O$$

Methyl alcohol is purified by refluxing with 1 per cent of calcium turnings (a calcium chloride guard-tube being placed in the end of the condenser to prevent access of moisture). Vigorous boiling is continued until the deposit becomes nearly white and the alcohol is then distilled into a dry receiver ($CaCl_2$ tube). The portion which comes over at constant temperature is again refluxed with 0·5 per cent of calcium turnings and is distilled into the dry flask which is to be used for the solution of the hydrochloric acid. The flask is weighed first and then again when about 250 ml. have been distilled into it. Carefully dried hydrochloric acid gas is next passed in until the gain in weight corresponds to that of a solution slightly more concentrated than 0·1 N. The concentration of the solution is determined by titration with standard barium hydroxide, using phenolphthalein as indicator, and is adjusted to exactly 0·1 N strength by the addition of pure methyl alcohol.

1·48 grams of pure dry cinnamic acid are weighed out and made up to 100 ml. in a measuring-flask with pure methyl alcohol. This solution is also titrated with barium hydroxide. The two solutions are now placed in the thermostat at 25° and left for 20 minutes. After this time 70 ml. of the cinnamic acid solution are run into a dry flask held in the thermostat and then 70 ml. of the hydrochloric solution are added. The time is noted as the zero time and the mixture is shaken; 30 ml. of the mixture is pipetted into each of four bottles, which are then replaced in the thermostat. At the end of each period of 2 hours from the zero time, one bottle is removed and its contents are titrated with the standard barium hydroxide. Each 30 ml. of the mixture contains 15 ml. of the cinnamic acid solution and 15 ml. of the hydrochloric acid solution. The number of millilitres of barium hydroxide required by the cinnamic acid at the start can be calculated from the preliminary titrations. This gives a in the equation; $a - x$ at the time t is obtained by subtracting, from the number of millilitres of barium hydroxide solution required to neutralize the 30 ml. of mixture at the time t, the number of millilitres known from the preliminary titration to be necessary for the 15 ml. hydrochloric acid solution which are present in the mixture. Using these values in the unimolecular-law equation the velocity constant is obtained. In this case the normality of the hydrochloric acid in the mixture is 0·5 ; if the velocity constant is divided by this factor we obtain the constant called the esterification constant for normal hydrochloric acid.

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[1] *Ber.*, 1899, *32*, 1691.

[2] *Rec. trav. Chem.*, 1935, *54*, 956.

(5) The Decomposition of Hydrogen Peroxide by means of Colloidal Platinum

$$2H_2O_2 = 2H_2O + O_2$$

A solution of colloidal platinum can be prepared by Bredig's method. Two pieces of stout platinum wire (2 mm.) are welded to thick copper wires. Pieces of glass tubing are fitted over the wires so that they can be handled ; the platinum of course projects from the ends of the glass tubes. The wires are then connected to the lighting circuit in series with a resistance to cut the current down to 5 amps. 20 ml. of conductivity water are placed in a dish and cooled by means of ice (externally). The platinum wires are brought into contact below the surface of the water and then separated 1 or 2 mm. thus establishing a short arc ; during the arcing, colloidal (and some larger) particles of platinum are driven off from the platinum. The arc persists for a short time only, and must then be re-made. This is continued for 10 or 15 minutes, and the solution is filtered to separate the coarse particles. 50 ml. of 20-volume hydrogen peroxide are diluted to 500 ml. with distilled water ; 250 ml. of this solution are placed in a flask in the thermostat and left for 20 minutes. 10 ml. are then removed, excess of dilute sulphuric acid added, and the mixture titrated with N/10 potassium permanganate. 5 ml. of the colloidal platinum solution are added and the time noted. The initial concentration of the peroxide solution is given by the number of millilitres of N/10 permanganate used, multiplied by $\frac{240}{245}$. 2 minutes after the start remove 10 ml. of the mixture, run it into excess of dilute sulphuric acid and titrate, noting the time of starting and the time of completing the titration and recording the mean of these two as the time of the titration. Repeat at intervals of 5 minutes. The concentration at any time t is proportional to the number of millilitres of permanganate required, so that these quantities can be inserted directly into the equation.

This reaction is also brought about by a photochemical method—the photochemical reaction of light of a wave-length less than 3,700 Å—a typical chain reaction. The analysis can be carried out by examining the absorption spectra of the products at different times during the reaction.

(1) Saponification of Ethyl Acetate by means of Sodium Hydroxide :

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH$$

The following solutions are required : N/60 ethyl acetate, N/40 sodium hydroxide free from carbonate, N/20 hydrochloric acid, and N/20 barium hydroxide. All solutions must be made up with distilled carbon-dioxide-free water. The ethyl acetate is redistilled and the middle fraction taken ; 1·467 grams are made up to a litre.

The sodium hydroxide is made up from metallic sodium, a piece of the metal of more than the weight required is taken, the oil removed from its surface and the outer layers cut off with a clean knife. The metal is then supported on a nickel gauze funnel over a platinum dish on a stand. This is covered as shown in Fig. 5 (IX^3) by a bell-jar standing in a dish of water containing caustic soda ; the top of the bell-jar is closed by a calcium chloride tube having its lower end bent so that no liquid can drop therefrom into the funnel or platinum dish. The sodium is thus in a moist atmosphere free from carbon dioxide, and it gradually dissolves and the caustic soda so produced drops into the platinum dish. When it has all dissolved the contents of the dish are made up to the required volume with carbon-dioxide-free water; the solution is then titrated against the standard acid and diluted with carbon-dioxide-free water to N/40. Two 750-ml. conical flasks of Jena glass are steamed out and dried. By means of pipettes 250 ml. of ethyl acetate solution are placed in one and 250 ml. of caustic soda in the other. Paraffined corks or glass stoppers are inserted and the flasks placed in the thermostat, where they are left for 20 minutes. The alkali is then added as quickly as possible to the ester solution and the mean time taken as the zero. The alkali remaining in the flask is washed down the sides and titrated with hydrochloric acid. This enables us to calculate the exact amount of alkali which was added to the 250 ml. of the ester, and also the alkali and ester concentrations of the resulting mixture (which is a little less than 500 ml. in volume). After 3 minutes 50 ml. of the mixture are

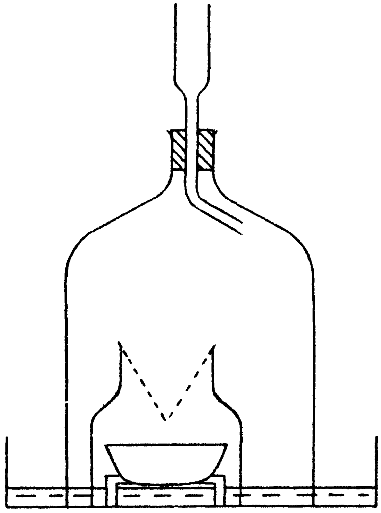

FIG. 5 (IX^3)
Reaction between sodium and water in an atmosphere free from carbon dioxide

withdrawn and run into 20 ml. of the N/20 hydrochloric acid solution, which stops the reaction. The time of the start and finish of the delivery of the solution from the pipette is taken and the mean taken as the time to be recorded. The excess of hydrochloric acid is titrated with N/20 barium hydroxide. The 20 ml. of acid are used by x ml. of barium hydroxide and y ml. of sodium hydroxide; x has been determined so that y, the caustic soda left in the reaction mixture, is calculated; knowing how much was originally present one can calculate the amount of sodium hydroxide used up and so the amount of ester used up and the amount of each left.

Further titrations are made at the end of 5, 10, 15, 30, 60, and 100 minutes, and the final titration 24 hours later.

Results. An example of Warder's results is given, when both substances were initially at a temperature of 26° and at a concentration of N/50:

Time in minutes	Alkali still remaining in ml. of N/8 acid required for 100 ml.	
5	10·24	5·625
15	6·13	5·37
25	4·32	5·405
35	3·41	5·27
55	2·31	5·385
120	1·10	5·645

The above measurement presents certain experimental difficulties due to the difficulty of preparing sodium hydroxide free from carbonate and the risk of absorption of carbon dioxide from the air during the reaction.[1] The reaction between ethyl bromoacetate and sodium thiosulphate:

$$CH_2BrCOOC_2H_5 + Na_2S_2O_3 = CH_2.NaS_2O_3.COOC_2H_5 + NaBr$$

is free from these disadvantages. It is very rapid in dilute solution. It can be followed by removing a portion of the reacting mixture from time to time and titrating with N/100 iodine solution, which only reacts with the unaltered thiosulphate. The experiment can be carried out with very simple apparatus. The following instructions give all essential details for the determination:

300 ml. of an approximately 0·17 normal solution of sodium thiosulphate at 25° is added to an equal volume of the dilute aqueous solution of ethyl bromoacetate at 25° in a 750-ml. flask. The flask is stoppered and the reaction allowed to proceed at 25°. At first every 5 minutes and then every 15 minutes 50 ml. of the reaction mixture is removed and titrated rapidly with standard iodine solution (N/100 approx.), using starch as indicator. Make 8 such titrations and after 5–6 hours (or overnight) a final titration to determine the excess of thiosulphate remaining. Determine the initial concentration of the thiosulphate by titration with iodine and determine the initial concentration of bromoacetate in the reaction mixture from the amount of thiosulphate eventually used up.

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[1] Slator, *Trans. Chem. Soc.*, 1905, *87*, 484.

(2) The Bromination of Cinnamic Acid :

$$C_6H_5CH:CH.COOH + Br_2 = C_6H_5CHBr.CHBr.COOH$$

This reaction is sensitive to light, so that either the thermostat must be in a dark room or the solution must be mixed in the dark room and transferred to amber-coloured bottles in which it can be kept in the thermostat and only again transferred back to colourless bottles for the titration.

Carbon tetrachloride is purified by washing with sulphuric acid, water, sodium hydroxide, and again water ; it is then allowed to stand over calcium chloride and is finally distilled from phosphorus pentoxide.

The bromine must be pure ; it is shaken with concentrated sulphuric acid, and after separation is frozen by means of ice and calcium chloride ; the solid bromine is separated, melted and again frozen until the melting-point becomes constant (− 7°) ; 1·233 grams of cinnamic acid are made up to 250 ml. with carbon tetrachloride and 1·333 grams of bromine are made up to the same volume with the same solvent. These solutions are accurately standardized, the acid with standard barium hydroxide (N/10), using phenolphthalein as indicator, and the bromine by the addition of excess of aqueous potassium iodide solution and titration of the liberated iodine with decinormal sodium thiosulphate, using freshly prepared starch solution as indicator. 20 ml. of the bromine solution are added to each of six stoppered bottles in the dark room and then 20 ml. of the acid solution. The bottles are stoppered and transferred to the thermostat ; one bottle is removed and its contents titrated by adding potassium iodide solution in excess and then thiosulphate. The concentration of the free bromine remaining is thus found, and since the initial concentration (N/60) is known, the amount of bromine used can be determined. Each molecule of bromine used corresponds to a molecule of cinnamic acid used, so that, since the initial concentration of this is known, the amount used can be calculated. If the initial concentrations of the two substances were the same (N/60) the calculation becomes very simple, since

$$\frac{dx}{dt} = k(a - x)^2$$

and
$$k = \frac{1}{t}\frac{x}{(a - x)a}$$

where a is the number of millilitres of thiosulphate required for the original solution at the start, $a - x$ is the number of millilitres required after time t, and x is the difference of these two.

Hydrolysis of Salt of Organic Base. As examples of practical applications of reaction velocities we may take the determination of the degree of hydrolysis of urea hydrochloride.

Methyl acetate is hydrolysed by water according to the equation

$$CH_3COOCH_3 + H_2O = CH_3COOH + CH_3OH$$

and this reaction is accelerated by acids. For a given acid the velocity constant divided by the normality of the acid is an approximate constant ; if this value has once been determined it can be used to find the normality of the acid. Now when urea hydrochloride is brought into the presence of water it is partially hydrolysed so that the solution contains some free hydrochloric acid; the urea hydrochloride solution will thus act as a catalyst on the methyl acetate reaction and so enable us to find the concentration of the free hydrochloric acid.

Methyl acetate is distilled and the bottle containing the distillate placed in the thermostat. N/2 hydrochloric acid is prepared and 100 ml. placed in each of two 250-ml. flasks in the thermostat. To one of these flasks 1·5 grams of urea is added so that this becomes an N/2 solution of urea hydrochloride. The N/2 hydrochloric acid should be titrated with barium hydroxide first. Then 5 ml. of methyl acetate are added to the flask containing the acid alone, the contents are quickly mixed, and 5 ml. are withdrawn and titrated at once with barium hydroxide solution. The preliminary test will show how much baryta solution will be required, remembering that the acid has been diluted 5 per cent by the methyl acetate; almost all the baryta can be run in at once and so the titration completed quickly; the mean time is noted. 5 ml. of the methyl acetate can then be added to the urea hydrochloride solution and the same procedure followed. Similar titrations are made at intervals of 10, 20, 30, 40, 60, 120 minutes, and 48 hours, and the velocity constants are calculated from the number of millilitres of baryta and the time, since the reaction is followed by the increase in acidity due to the liberation of acetic acid.

Now, if k_1 is the value found for the velocity constant for hydrochloric acid alone and k_2 is the value for urea hydrochloride, the fraction of urea hydrochloride hydrolysed in an N/2 solution is $h = \frac{k_2}{k_1}$.

Strengths of Acids. The same reaction can be used to find the relative strengths of acids since the catalysis is actually proportional to the hydrogen ion concentration. We have then, for example, to take 100 ml. each of N/2 hydrochloric acid and N/2 sulphuric acid, add to each 5 ml. of methyl acetate, determine the velocity constants as above, and the relative strengths of the acids used will be

$$\frac{\mathrm{HCl}}{\mathrm{H_2SO_4}} = \frac{k_{\mathrm{HCl}}}{k_{\mathrm{H_2SO_4}}}$$

Reversible Reactions. Wilson and Dickinson[1] have measured the reaction rates of this type, namely the oxidation of arsenious acid by iodine at equilibrium as well as the reverse reaction rate at equilibrium. This reversible reaction may be expressed as follows:

$$\mathrm{H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI}$$

it was first investigated by Roebuck[2] by customary methods. Wilson and Dickinson applied a new method of investigation using radioactive indicators. Their procedure was as follows:

A radioactive arsenic with a half-period of 26 hours is formed from ordinary arsenic by neutron capture. To utilize this Wilson and Dickinson exposed 15 to 20 grams of pure crystalline arsenic for 2 to 3 days to a radon-beryllium source of neutrons whose initial strength was 200 to 300 millicuries; the exposure occurred in a large block of paraffin. The arsenic was then burned to arsenious oxide in a stream of air and a weighed amount of oxide dissolved in a measured volume of 1 N standard sodium hydroxide solution, which was then diluted to the desired concentration. The reaction mixtures were then prepared from standard solutions of arsenic acid, hydrochloric acid, and the radioactive arsenite.

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[1] *J. Amer. Chem. Soc.*, 1937, *59*, 1358.

[2] *J. Phys. Soc.*, 1902, *6*, 365.

The mixtures were brought to thermostat temperature and a measured volume of standard potassium iodide at the same temperature was added. The mixtures were such that at equilibrium comparatively little free iodine should be present. The colour due to free iodine developed immediately on the addition of the potassium iodide and became constant within a minute or two, indicating a rapid approach of equilibrium.

The solutions were kept at constant temperature for a measured period of from 4 to 17 hours. During this period exchange of radioactive arsenic between the tri- and pentavalent states occurred presumably through reactions with iodide and iodine. The exchange was then quenched by dilution with water and addition of an excess of ammonium hydroxide sufficient to make the solution 0·6 N in the latter reagent. The arsenate was then immediately precipitated as magnesium ammonium arsenate by the addition of magnesium-ammonium nitrate solution. The precipitate was washed with 0·6 N ammonium hydroxide, filtered, dried, and ignited to magnesium pyroarsenate which was then ground to a fine powder.

A fixed weighed amount of the powder was placed in a shallow cylindrical depression 0·1 cm. deep and 5 cm. in diameter in a thick sheet of brass; the powder was pressed down to fill the depression fully and evenly. The brass sheet was then placed in a reproducible position under a quartz fibre electroscope and the activity of the arsenic measured.

About one-fifth of the original radioactive arsenite solution was oxidized to arsenate with sodium hypobromite and was then precipitated, ignited, and its activity measured just as with the exchange samples. All activities were corrected to the same time using the half-period 26 hours.

Wilson and Dickinson [1] summarized their results as follows: Radioactive trivalent arsenic does not exchange with non-radioactive pentavalent arsenic in dilute acid or alkaline solutions in the absence of other easily oxidizable or reducible substances. In the presence of iodine in acid solution, however, an exchange takes place at a measurable rate. On the assumption that the exchange occurs through the oxidation and reduction of the iodine, the rates of oxidation and reduction at chemical equilibrium from measurements of rates of exchange in systems containing iodide ion and small amounts of free iodine were calculated. The rates of oxidation and reduction measured in this way are in agreement with the kinetic expressions shown by Roebuck to hold for the same reactions remote from equilibrium, and lead to specific rate constants which agree with those measured by him.

Influence of Solvent on Rate of Reaction

The rate of decomposition of nitrogen pentoxide is influenced by the nature of the solvent present. For other reactions there is not much experimental data on this subject. The apparatus used by Eyring and Daniels [2] for such work is shown in Fig. 6 (IX[3]). It is a modification of an apparatus previously used by Lueck.[1] A flask of 5 ml. capacity containing the nitrogen peroxide in solution was connected to the gas burette through a coil of thin-walled glass tubing 1 ml. in diameter and about 1 metre long. The glass tube had sufficient flexibility to permit rapid shaking of the solution in a pendulum cradle. The flask contained two or three glass pearls to assist in agitating the liquid. The solution was introduced through the side-arm, which was then sealed off. The flask was placed in the thermostat and strapped to the shaker. The burette was filled with nitrobenzene, which was drained out as needed to maintain the level in the two arms. Before reaching the burette the oxygen passed through glass-wool saturated with concentrated sulphuric acid to remove any nitrogen dioxide. The flask was made small to economize nitrogen pentoxide and to minimize any error due to the partial pressure of nitrogen produced by the decomposition.

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[1] *Loc. cit.*

[2] *J. Amer. Chem. Soc.*, 1930, *52*, 1472.

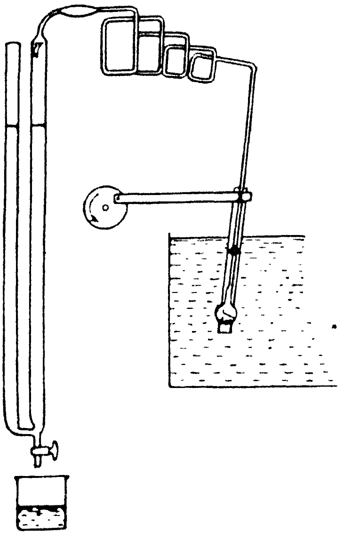
FIG. 6 (IX³)
Apparatus for the determination of the gaseous decomposition products of nitrogen pentoxide

Temperature. A thermoregulator with oscillating contact kept the temperature of the thermostat within 0·01°. The shaker operated through an arc of 10 cm. 360 times per minute and it was shown by experiments that this agitation was ample to prevent supersaturation of the solution with oxygen.

A thermocouple inserted in the solution showed that at 600 oscillations the temperature of carbon tetrachloride in the flask at 45° was raised 0·0277° by the mechanical shaking but at 360 oscillations it was raised less than 0·02°. The thermocouple gave a zero reading when the shaker was stopped. This temperature rise makes a difference of less than 1 per cent in the reaction rate and is within the limit of experimental error. The heating was slightly less when the nitrogen pentoxide was decomposing, due probably to the evaporation of the solvent by the escaping oxygen gas.

The specific reaction rate k is given by the equation used by Timmermans and Martin[2]

$$k = \frac{2 \cdot 303}{t_2 - t_1} \log \frac{V_\infty - V_1}{V_\infty - V_2}$$

in which V_1 is the volume of oxygen liberated at time t_1, V_2 is the volume at time t_2 and V_∞ is the final or total volume.

Solvent Effect. Part of the data for different solvents as obtained by Eyring and Daniels[3] are given in the table. In these experiments the concentration was kept the same, approximately one-thousandth of a mole in 5 ml. of solution, corresponding to a calculated osmotic pressure of about 5 atmospheres.

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[1] *J. Amer. Chem. Soc.*, 1922, *44*, 757.

[2] *J. Chim. Phys.*, 1926, *23*, 733; 1928, *25*, 251.

[3] *Loc. cit.*

SPECIFIC DECOMPOSITION RATE OF NITROGEN PENTOXIDE IN DIFFERENT SOLVENTS

Solvent	Values of $k \times 10^4$			
	15°	20°	25°	40°
Nitrogen tetroxide	0·159	0·344	—	—
Ethylidene chloride	—	0·322	—	4·22
Chloroform	—	0·274	0·554	3·78
Ethylene chloride	—	0·238	0·479	3·70
Carbon tetrachloride	—	0·235	0·469	3·62
Pentachloro-ethane	—	0·220	0·430	3·26

SECTION 5: COURSE OF REACTION

For a great many reactions between non-volatile solids no special apparatus is necessary for studying the course of the reaction. Samples are taken from the solution in the thermostat and estimated as soon as possible, preferably with cooling and/or dilution to stop the reaction. An apparatus of general application suitable for following the course of rapid chemical reaction in solution has been described by Powell and Trendall.[1] The apparatus was devised by the authors in connexion with an investigation into the rates of hydrolysis of alkyl halides and they recommend it in kinetic studies generally whenever it is possible to follow a reaction by direct titration *in situ*. Velocity constants as high as 1·7 min.$^{-1}$ have been successfully measured with it. The following is the authors' description of the method:

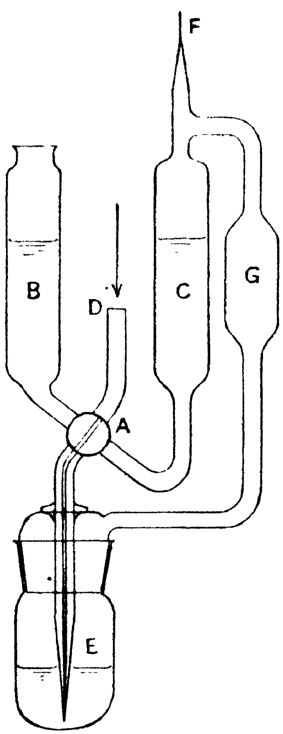

FIG. 7 (IX[3])
Apparatus for study of rates of reaction—by direct titration *in situ*

The principle of the device consists in adding to the reaction mixture, containing an indicator, small constant amounts of a standard solution determined by the bore of a tap. In Fig. 7 (IX[3]), A is a four-way tap whose key has a single straight bore of which the volume is of the order of 0·02 ml. Two arms are connected to reservoirs B and C for standard reagent, D is supplied with air under a few inches water-pressure (e.g. from a filter-pump-aspirator blower) and the remaining arm, of capillary bore, passes through a ground joint to the bottom of the reaction vessel E. A lead from the top of the latter communicates via a bulb G with the top of reservoir C, which is provided with an air leak at F.

With the bore of the tap in the position shown, air bubbles through the solution in E, stirring it, and escapes at F, which is fine enough to ensure an appreciable rise in pressure in C. When now the tap is turned through a right angle, its bore is positively cleared of air by a flow of liquid from C to B; this takes but a moment, and then as the excess pressure is relieved by the leak F (the air supply being now cut off) the level in the reservoirs is restored after a few seconds. The bore is now charged; its contents are driven into E and stirred by turning the tap to its original position, and so on. The bulb G serves to increase the air capacity when the reservoirs are full.

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[1] *J. Soc. Chem. Ind.*, **1943**, *62*, 368.

Two points should be noted in connexion with the glasswork: first, the bore of the tap should register fairly accurately with the holes in the barrel, and in particular should meet the surface of the key in sharp edges; second, the drainage error is minimized by keeping the tube leading from A into E undistorted at the internal seal. This is done by forming a short tube on the cover of the reaction vessel which is a close fit over the leading-in tube. The latter need not then be blown when the two are fused together.

Calibration of the tap can of course be carried out by weighing, but it is preferable to calibrate tap and reagent together by titrating a quantity of a suitable known standard solution in the reaction vessel. A little of the standard is put into the latter and brought to its end-point, to avoid initial drainage error, then an exactly measured volume. The accuracy of the estimation will depend on the number of turns of the tap required to neutralize this amount; the equivalent of half a turn can easily be estimated, and after the standardization has been carried out for the first time the quantity of solution to be titrated can be judged according to the precision desired. It is important always to keep the tap open to the reaction vessel for a fixed period before turning it back; 3 or 4 seconds is enough, and a suitable number of revolutions of the thermostat stirrer can be counted to mark this time.

In carrying out an experimental run the same drainage period must be adhered to. The components of the reaction, with the indicator, are mixed in the vessel E which is then immediately attached to the upper part of the apparatus; an addition of standard reagent is made and when the indicator changes the time is noted and a further addition made. This cycle of operations can, if necessary, be repeated up to about 10 times a minute; thus quite rapid reactions can be followed comparatively easily. The concentration of the standard reagent is adjusted according to the speed of the reaction under investigation, the degree of completeness to which it is desired to follow it, and the amount and concentration of the reaction mixture. The large number of point data obtained will determine a velocity constant with considerable certainty, or serve to test fairly stringently the law corresponding to an hypothetical mechanism.

It was found that the tap could be lightly greased without prejudice to its constancy of delivery. In order to test the latter, weighings of single deliveries, of groups of two, and of groups of five were carried out. The coefficients of variation in the three sets were 9·33 per cent, 2·81 per cent, 1·15 per cent respectively. These are in the ratio 1 : 0·30 : 0·12—much less than that to be expected on purely statistical grounds—1 : 0·71 : 0·45. The drainage error is thus largely self-compensating; the present figures include an error due to differing amounts of liquid left on the tip of the leading-in tube, and in practice the variations may be expected to be rather smaller.

Fig. 8 (IX^3) representing the hydrolysis of acetic anhydride at 0° is given as an example.[1] Here 10 ml. of a 0·01 N solution were used, and the acid production followed by titration with 0·1 N baryta, with bromthymol blue as indicator.

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[1] Powell and Trendall, *ibid.*

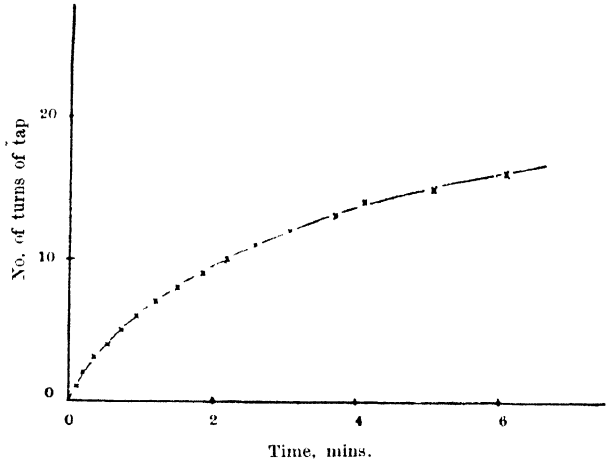

FIG. 8 (IX³)
Hydrolysis of acetic anhydride at 0°

Other Methods of Following Reactions

In cases other than that on non-volatile solids special precautions are sometimes necessary in studying the course of chemical reactions. Difficulties occur with gases, with solutions of volatile liquids in a third liquid, in reactions where the extent of the change may be difficult to measure by purely chemical methods, and in very fast reactions. Typical methods introduced for dealing with such cases are the following:

The Sealed Bulb Technique. Portions of the solution to be investigated are sealed off in glass tubes, which are then placed in the thermostat for known times, cooled, opened, and the contents analysed. It is essential that the free space above the liquid should be as small as possible, since volatilization, especially at fairly high temperatures, may seriously affect the results if the free space is large. This method has been used by Moelwyn-Hughes and Hinshelwood [1] to study the decomposition of chlorine monoxide in carbon tetrachloride, and by Moelwyn-Hughes [2] in an investigation of the uncatalysed hydrolysis of the methyl halides in water.

The apparatus of Moelwyn-Hughes [3] for the preparation of the solutions of the methyl halides is shown in Fig. 9 (IX³). Ordinary distilled water, which separate experiments showed to be as suitable as the purest conductivity water, is sucked into the 500-ml. bulb A, where it is vigorously boiled at 20°. The vapour of the methyl halide, stored in the 3-litre bulb B, is led over anhydrous calcium chloride into the water in A, where it is allowed to bubble slowly for a day or two, pending saturation. After measuring the partial pressure of the methyl halide, the solution is delivered into graduated reaction vessels by letting in air gently and at equal rates to both limbs of the bubbler; agitation of the solution leads to loss of solute vapour. The sealed tubes are placed separately in pairs of concentric metal cylinders of the type described by Moelwyn-Hughes and Hinshelwood.[4] After immersion for a measured time in electrically regulated or in boiling-vapour thermostats, the contents of each tube are analysed for halide and hydrogen ions and for free halogen. The end-point of each run corresponds to complete hydrolysis according to the equation

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[1] *Proc. Roy. Soc. A.*, 1931, *131*, 177.

[2] *Ibid.*, 1938, *164*, 295.

[3] *Ibid.*

[4] *J. Chem. Soc.*, 1933, 1567.

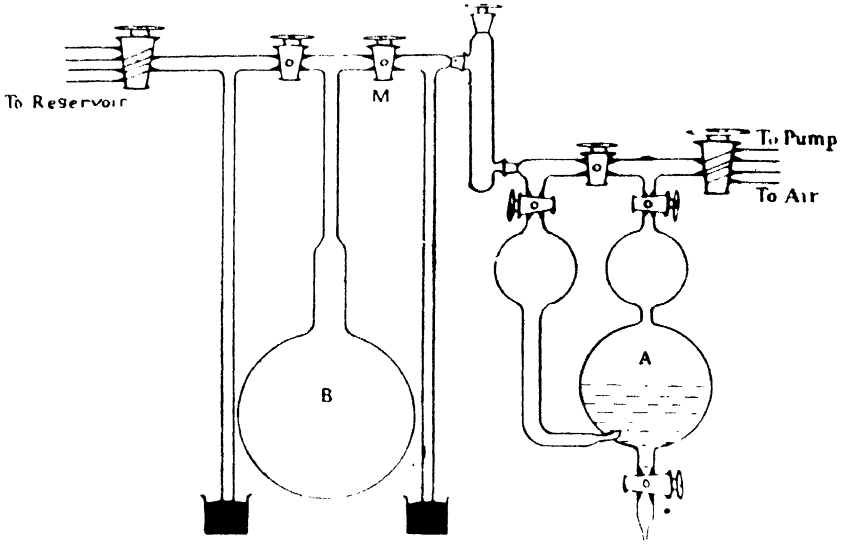

FIG. 9 (IX³)

Apparatus for the preparation of solutions of the methyl halides

$$CH_3X + H_2O \rightarrow CH_3OH + H^+ + X^-$$

Due, however, to an inevitable escape of some solute vapour, the first tube of a series to be filled usually required rather more analytical reagent than the last, but the loss seldom exceeded 1 per cent. That the end-points correspond to complete hydrolysis was shown by treating the hydrolysed solutions with alcoholic potash or with aqueous silver nitrate when no further change could be detected.

Dilatometric Method. Where a reaction is accompanied by a change in volume, a dilatometer offers a very convenient method of following its course. The usual form of dilatometer consists essentially of a bulb with a capillary tube at the top and tap at the bottom for filling. Small leaks at the tap are a constant source of danger, and Benford and Ingold [1] describe several improved types in which the tap is eliminated (Fig. 10 (IX³)).

A is the ordinary type in which filling is accomplished through a funnel. In B the upper capillary is made of very small diameter (0·04 cm.) to give increased sensitivity, and the dilatometer is filled by attaching one arm to a vacuum pump, the opposite limb dipping into a beaker containing the reaction mixture. Dilatometer C permits the stirring of the contents of the bulb with a small iron rod enclosed in a Pyrex tube.

Another modification, type C, permitted the stirring of the contents of these dilatometers. The bulb was inclined with its axis making an angle of 25° with the vertical direction, and 2 in. of $\frac{1}{8}$ in. round malleable iron rod, enclosed in a Pyrex glass tube, was included in the bulb when the instrument was being made. This stirring-rod was actuated by an electromagnet, fed with interrupted direct current. The magnet was soldered into a brass case for immersion in the thermostat alongside the dilatometer, the electric leads passing out through a brass tube. The interrupter was of simple brush-and-sector design, the sector-wheel being driven by a variable-speed motor. With this arrangement the speed of stirring could be varied between 25 and 250 strokes per minute.

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[1] *Ibid.*, 1938, 929.

Calibration of Dilatometers. The capillaries were calibrated by a method depending on the thermal expansion of a liquid. In almost every case, the corrections for variations of bore proved negligible, and it was in practice unnecessary to read more than one limb of the instrument: in other words, the dilatometer constant was the same for all parts of the single scale.

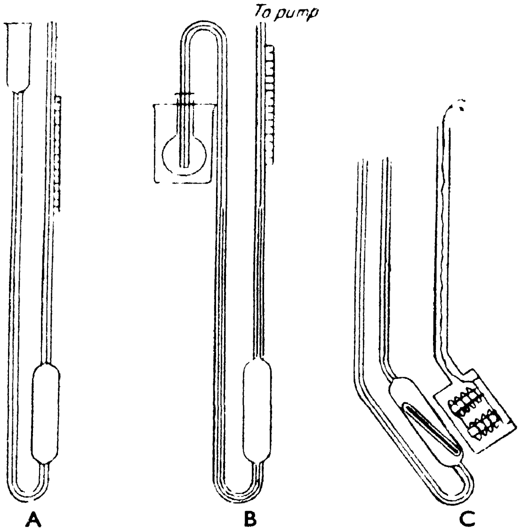

FIG. 10 (IX^{a})
Improved forms of dilatometer suitable for measuring changes in volume during a reaction

The dilatometer constants were determined by observation of the thermal expansion of conductivity water in an adjustable precision thermostat, a Beckmann thermometer being used for the measurement of temperature differences. Correction was made for the thermal expansion of the glass. The temperature correction for the dilatometer constant, calculated from the coefficient of expansion of the glass, was negligible.

In all cases the bulb should be of small diameter and of the thinnest possible glass, to ensure rapid heat exchange between the contents and the thermostat. Previous calibration (e.g. with conductivity water) is essential in order to allow for possible inequalities in the bore of the capillaries. The movement of the liquid on the scale can be followed through a telescope if desired.

In the study of vinyl acetate polymerization Starkweather and Taylor[1] used the dilatometer method to follow changes in volume during polymerization. The method has been employed also by Cuthbertson, Gee, and Rideal[2] to follow effect on polymerization of vinyl acetate by peroxide catalysts. The vinyl acetate was fractionated until a portion of the distillate gave only a barely perceptible pink coloration with Shiff's reagent on standing 5 minutes. This material showed practically no tendency to polymerize up to a temperature of 100° over a period of 24 hours. The reaction was followed by observing the contraction of 5-ml. samples sealed *in vacuo* in well-cleaned dilatometers constructed from short lengths of burette tubing, Starkweather and Taylor having shown the volume contraction to be directly proportional to the extent of polymerization. The meniscus became distorted when the reaction was nearly complete, rendering the late readings inaccurate. Measurements were carried out with pure vinyl acetate at 60°, 80°, and 100° and in toluene solutions (40 and 17 per cent) at 80° over a wide range of catalyst concentrations. The toluene used was free from sulphur-containing bodies, some of these being effective inhibitors. The 100° results are given in the following table and indicate the order of experimental accuracy.

POLYMERIZATION OF VINYL ACETATE CATALYSED BY BENZOYL PEROXIDE AT 100°

Time in min.	Experiment in Catalyst conc. in mol./l.: Per cent Polymerization			
	A $82{\cdot}6 \times 10^{-6}$	B $20{\cdot}7 \times 10^{-6}$	C $6{\cdot}9 \times 10^{-6}$	D $2{\cdot}3 \times 10^{-6}$
9·5	2·5	—	—	—
14	8	—	—	—
15	13	—	—	—
18	15	—	—	—
22	20	1·5	0·5	—
26	26	—	—	—
28	27·5	4	—	—
32	32·5	6·5	1·5	—
37	35·5	7	3	—
43	39	9	4	—
48	41	11·5	4·5	—
55	45	13	—	—
61	45·5	14·5	5	—
67	47	15·5	6	—
75	49	18	7	2·5
85	52	19·5	8	3
95	52·5	21	10·5	4
105	54	22	—	—
125	57	24·5	11	5
181	58·5	26	13·5	7
232	—	—	15·5	10·5
402	60	32·5	18	13

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[1] *J. Amer. Chem. Soc.*, 1930, *52*, 4708.

[2] *Proc. Roy. Soc. A.*, 1939, *170*, 300.

It will be noted that in all cases a period of induction is observed, and that in a number of cases with small catalyst concentrations the reaction comes to an end before polymerization is complete.

Use of Optically Active Substances. The rate of formation of polymers has been examined by Marvel, Dee, and Cooke,[1] using an optically active vinyl derivative as the monomer and following the optical changes during the polymerization. The reaction was carried out in a special polariscope tube 176 cm. long of Pyrex glass with an electrically heated oil-jacket. The end-plates of optical Pyrex glass were sealed to the tube with 'Sauereisen Cement'. A coil of nichrome wire which had a resistance of 1 ohm per foot was placed in the outer oil-jacket and connected through a rheostat. The resistance was adjusted so that the oil-jacket was maintained at 60°. When the tube was heated, sufficient strain was put on the optical end-plates so that readings could not be made. Hence, it was necessary to heat the polymerization mixture a definite time, cool rapidly to room temperature (25°), take a reading and then repeat the process.

Rapid Chemical Reactions. An apparatus has been devised by Du Bois for the study of the kinetics of certain rapid chemical reactions.[2] It is a modification of that described by Thiel and Longemann [3] and is based on the Hartridge-Roughton [4] flow principle using a glass 'observation tube' connected with a small mixing-chamber. The two solutions that are to react converge in the mixing-chamber and the mixture flows through the observation tube. According to Du Bois [5] if the reaction results in a change of colour and if the flow along the tube is at a suitable and constant rate, the change of colour occurs while the liquid is passing through the observation tube and the gradation of colour along the tube remains fixed in position. If the rate of flow is known, the reaction time at any point along the tube may be calculated from its distance beyond the point of mixing. Colorimetric measurements by a photo-cell can be made at a number of points along the tube and a curve showing the kinetics of the reaction may be plotted. This procedure requires a fairly large amount of material and is satisfactory for substances such as haemoglobin that can be readily obtained in quantity. Furthermore, since each point on the curve requires a separate experiment, the method is somewhat laborious.

For details of the apparatus the original paper of Du Bois should be consulted.[6] The novel features of the apparatus as recorded by the author are as follows:

1. The observation tube moves vertically through a fixed beam of monochromatic light so that the light scans the tube during the reaction.
2. The observation tube is formed with bars of transparent plastic, and the ducts which carry the reactants to the point at the base of the observation tube, where they mix, are cut or drilled in this plastic material.
3. The process of mixing has been studied by various optical methods, including the schlieren method, and from a number of mixing arrangements

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[1] *J. Amer. Chem. Soc.*, 1940, *62*, 3499.

[2] *J. Biol. Chem.*, 1941, *137*, 123.

[3] *Sitzungsber. Ges. Beförder ges Naturwissensch.*, Marburg, 1934, *69*, 102.

[4] *Proc. Roy. Soc. A.*, 1923, *104*, 376.

[5] *Loc. cit.*

[6] *Loc. cit.*

tried one has been selected which gives satisfactory mixing. This mixer is built on the homogenizer or colloid mill principle.

4. A double-wedge calibrating device is used to trace a calibration curve of the apparatus as a whole.

5. As the apparatus functions, small lights flash, and make fiducial marks on the edges of the photographic record. These marks together with the reaction curve complete the data necessary for a calculation of the kinetics of the reaction under study.

A recording apparatus employing the ' accelerated ' and the ' stopped ' flow principle for the study of rapid reactions has also been described by Chance.[1]

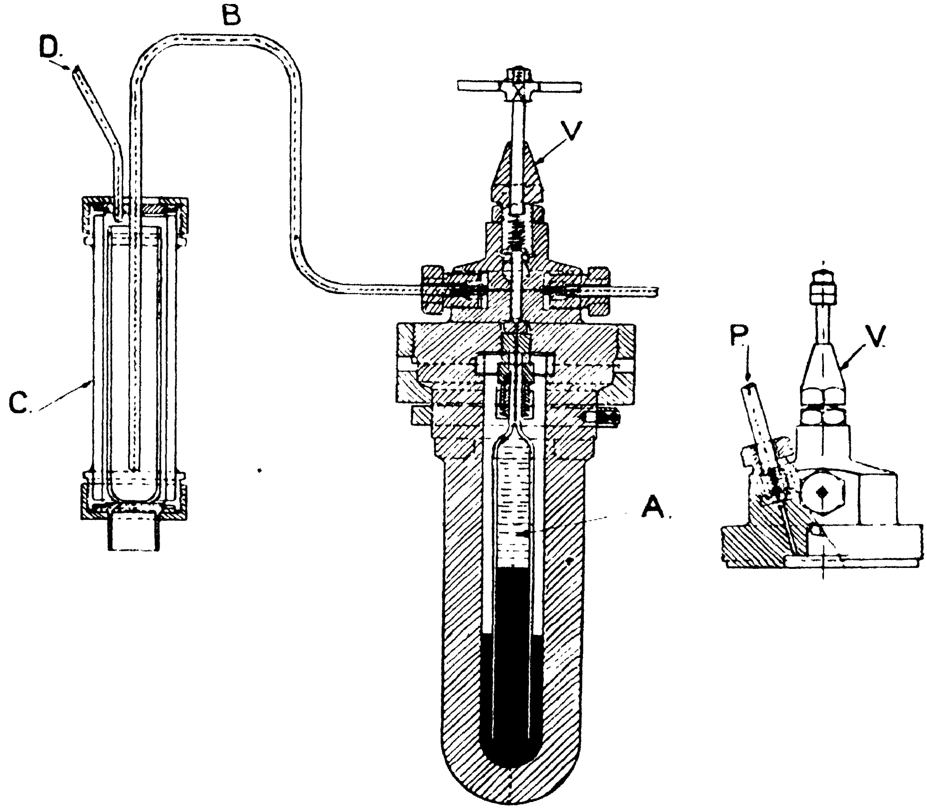

FIG. 11 (IX[3])

Apparatus suitable for the study of reactions in solution at high pressures

Very Fast Reactions. The monolayer technique worked out by Alexander and Rideal [2] opens up a new method of approach to the study of reactions which in the bulk phase take place much too rapidly to be measured by ordinary methods. Thus the very fast substitution of bromine in the nucleus of substituted phenols has been followed [3] by spreading a layer of a long chain phenol (p-hexadecylphenol) on a substrate of bromine water (10^{-4} M) and following the changes of surface pressure and surface potential as the reaction proceeded.

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[1] *J. Franklin Inst.*, 1940, *229*, 455, 613, 737.

[2] *Proc. Roy. Soc. A.*, 1937, *163*, 70.

[3] *J. Chem. Soc.*, 1938, 729.

Reactions under Pressure. At comparatively low pressures, corresponding to a temperature of 20°–30° above the boiling-point of the solvent used, the sealed-bulb method may be used, with precautions to make the free space as small as possible. For work under pressures of the order of several thousand kg./cm.[2] special apparatus is necessary. Gibson, Fawcett, and Perrin [1] have designed plant suitable for the study of reactions in solution at pressures up to 300 kg./cm.[2], with provision for removing samples for analysis from time to time (Fig. 11 (IX[3])).

The reaction mixtures (sodium ethoxide and ethyl iodide in alcohol, and pyridine and ethyl iodide in acetone) were contained in the glass bell A, of about 120 ml. capacity, which was attached by means of a packing gland to the high-pressure side of a valve, B, built into the head of the steel pressure vessel as shown. Pressure was transmitted to the reaction mixture by a light lubricating oil through the lead P, which was connected to a Cailletet-type screw press, and measured with a Bourdon gauge, frequently checked against a calibrated pressure balance. Before starting an experiment, the reaction mixture was placed in a tube in the glass cylinder C, and forced into the bell A, through the nickel tube B by compressed air applied at D. The valve V was then closed and the oil pressure applied. The second lead of the valve V was normally closed by a valve (not shown), and this lead enabled the tube B to be cleaned after use. When required, samples were drawn off through B, by opening the valve V, during which time the pressure in the vessel was maintained by means of the screw press. When the reaction was studied at temperatures above the boiling-point of the solvent at atmospheric pressure, a cylinder was placed inside the tube C for the sample, and air pressure applied at D, in order to prevent evaporation in the leads. The pressure vessel was placed in a thermostat controlled to 0·1° at the required temperature.

At still higher pressures the apparatus described and illustrated in Vol. I, p. 344, was used, but in this case samples could only be withdrawn at the end of the reaction.

Reactions between Gases. The number of gas reactions is legion, and the types of apparatus used by different workers correspondingly diverse. Important possible complications are heterogeneous reactions catalysed by the surface of the reaction vessel, and chain reactions. A clue as to their presence or otherwise is provided by loosely packing the reaction chamber with glass wool, the increased surface of which leads to an increase of rate in heterogeneous reactions, but as a rule to a slowing down of changes in which a chain mechanism is involved.

A good example of the application of these factors is the reaction

$$2NO + Cl_2 = 2NOCl$$

as studied by Stoddart.[2] Complications in this reaction are caused by surface effects and by the interaction of the gases with the mercury of the manometer. The apparatus was designed to eliminate these factors as far as possible.

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[1] *Proc. Roy. Soc. A.*, 1936, *150*, 223.

[2] *J. Chem. Soc.*, 1940, 823.

The apparatus was constructed throughout in soda glass, and was cleaned with alcohol-nitric acid, washed and dried before assembly. Before making each run the whole apparatus was evacuated for several hours by a ‘ Hyvac ’ pump, following which the pure gases were allowed to stream through the holding vessels B and C for several hours longer. Each of the vessels A, B, and C was of about 750 ml. capacity, and when B and C contained pure gas the taps F and H were shut and the whole apparatus placed in a thermostat. The reaction vessel A could be placed in communication with a glass-spring tensimeter D, this being used as a null instrument enabling the pressure in A to be measured without allowing the gases to come in contact with the mercury of the manometer.

When the gases in B and C had attained the temperature of the thermostat one of the gases was introduced into A and its pressure measured. Then the second gas was introduced and the total gas pressure measured as quickly as possible. As the reaction proceeded, the pressure was recorded by adjusting the gas pressure in the outer jacket of the tensimeter by the tap K, till the needle returned to its zero position. The pressure in the reaction vessel A was then that in the jacket, which was directly read off the mercury manometer and could be checked by momentarily connecting A directly to the manometer through the tap L.

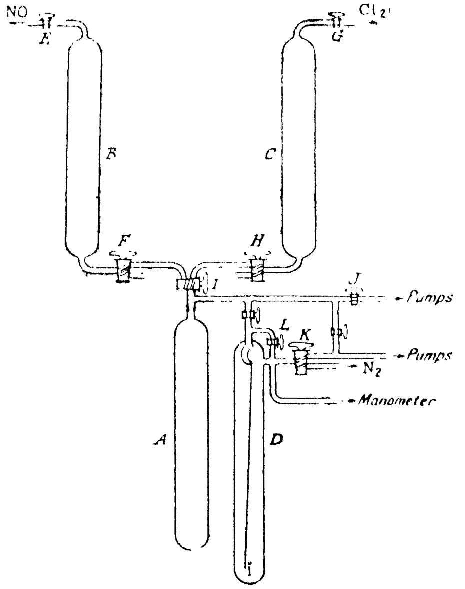

FIG. 12 (IX[3])
Apparatus for reaction between gases

All the taps and tubing were made of large (6 mm.) bore to facilitate evacuation and rapid mixing of the gases. Apiezon grease was used as a lubricant, other lubricants being found to react with the chlorine and the nitrosyl chloride.

The effect of increased surface was studied by packing the reaction bulb with glass tubing to give a tenfold increase of surface per c.c. of gas.

It was found that the termolecular homogeneous reaction postulated by the equation does not occur in practice under the conditions of these experiments. The reaction velocity is considerably influenced by surface conditions, and the nitrosyl chloride can seriously inhibit the reaction by adsorption on the surface of the vessel.

The unimolecular dissociation of gaseous ethyl bromide investigated by Vernon and Daniels[1] is of interest for a number of reasons. At the temperature used (395°–420°) a thermostat of molten lead was necessary, the temperature of which was controlled by a relay actuated by a photo-electric cell on to which a beam of light from the galvanometer mirror was reflected. All-glass or all-quartz vessels were used, totally immersed in the bath, the pressure being followed by a special manometer in which the pressure of vapour was balanced against a known air pressure through a glass diaphragm. The point of balance was obtained by closing an electrical circuit through a platinum contact fused to the diaphragm.[1] (Full constructional details, and a useful bibliography on various types of diaphragm manometers, are given in the original paper.)

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[1] *J. Amer. Chem. Soc.*, 1933, *55*, 922.

Special precautions were taken to remove air and to obtain glass surfaces completely free from deposited carbon, and absolutely pure ethyl bromide was used. Observance of these precautions gave a high degree of reproducibility to the velocity constant of the reaction, which was shown to be homogeneous by the unchanged rate of reaction when powdered glass was added.

The calculation of k was considerably complicated by the occurrence of the reverse bimolecular reaction

$$C_2H_4 + HBr = C_2H_5Br$$

The original paper gives full details of the mathematical methods of overcoming this difficulty.

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[1] *Ibid.*, 1928, *50*, 1115.

SECTION 6: ORDER OF A REACTION

Various methods have been employed for determining the order of a reaction. The most important of these methods are summarized in this section.

(1) **Direct Method.** The rate of reaction is measured by suitable means at given intervals of time, and the results substituted in the equations for the velocity constant for first, second, &c., orders. Of the values of k so obtained one series will usually show more constancy than the rest. The method is unsatisfactory when complicating side reactions occur.

(2) **van 't Hoff's Differential Method.** If the differential $-\frac{dC}{dt}$ can be measured with different initial concentrations C_1 and C_2, and the number of molecules taking part in the reaction is n,

$$-\frac{dC_1}{dt} = kC_1^n$$

$$-\frac{dC_2}{dt} = kC_2^n$$

Taking logarithms and subtracting,

$$n = \frac{\log\frac{dC_1}{dt} - \log\frac{dC_2}{dt}}{\log C_1 - \log C_2}$$

The differential $\frac{dC}{dt}$ may sometimes be obtained with sufficient accuracy from the small finite differences in time and concentration $\frac{\Delta C}{\Delta t}$.

(3) **The 'Half-life' Period Method.** A more practical way of examining this method may be seen from the following observations:

For first-order reactions

$$kt = ln\frac{a}{a-x}$$

At the half-life period τ,

$$\tau = \frac{1}{k}ln2$$

Similarly for reactions of the second order, where the initial concentrations of the reactants are equal

$$kt = \frac{x}{a(a-x)}$$

and the half-life is given by

$$\tau = \frac{1}{ka}.$$

In general, in a reaction of the nth order, the half-life is inversely proportional to the $(n - 1)$th power of the initial concentration, as can easily be shown. Hence the order of a reaction can be judged from a study of the effect of change of initial concentration on the period of half-life. The two examples given below [1] illustrate the application of the method to the first-order thermal decomposition of phosphine and to the thermal decomposition of nitrous oxide, which at ordinary pressures is more nearly of the second order than of any other. Here a is equal to the initial pressure of the gas, and K is assumed constant in calculating the third column (C).

THERMAL DECOMPOSITION OF PHOSPHINE

Initial pressure (a) in mm.	Half-life in seconds (T)
707	84
79	84
37·5	83

THERMAL DECOMPOSITION OF NITROUS OXIDE

Initial pressure (a) in mm.	Half-life in seconds (T)	C
296	255	75·3
139	470	65·3
52·5	860	45·2

For the first-order decomposition of phosphine the figures show that no correlation exists between the half-life and the initial pressure. On the other hand, the decomposition of nitrous oxide is shown to be approximately bimolecular from the fact that the half-life is roughly in inverse proportion to $\frac{1}{a}$.

(4) **The Method of Finding the Times required for Equal Fractional Decreases of Concentration.** Two experiments are made with respective initial concentrations of C_1 and C_2:

C_1 decreases to C_1' in time t_1
C_2 decreases to C_2' in time t_2

C_1 and C_2 are so chosen that

$$\frac{C_1' - C_1}{C_1} = \frac{C_2' - C_2}{C_2}$$

Then
$$\left(\frac{C_2}{C_1}\right)^{n-1} = \left(\frac{C_2'}{C_1'}\right)^{n-1} \text{(Ostwald)}$$

and if the action follows the same course throughout

$$n = 1 + \frac{\log t_1 - \log t_2}{\log C_2 - \log C_1}$$

(5) **The Isolation Method.** From the equation

$$-\frac{dC}{dt} = k(C_1^{n_1} \times C_2^{n_2} \times C_3^{n_3})$$

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[1] Hinshelwood, *The Kinetics of Chemical Changes*, Oxford Univ. Press, 2nd ed., 1942. This book should also be consulted for an excellent account of the theoretical aspect of the subject.

if C_2 and C_3 are made very large compared with C_1 the former may be regarded as constant and $-\frac{dC}{dt} = kC_1^{n_1}$ so that the exponent n_1 can be determined. In a similar way n_2 and n_3 are obtainable. As an example we may take the determination of the order of the reaction of hydriodic acid on bromic acid:

$$6HI + HBrO_3 = HBr + 3H_2O + 3I_2$$

Decinormal solutions of potassium iodide, potassium bromate, and hydrochloric acid are required, and an N/100 solution of sodium thiosulphate.

25 ml. of iodide, 100 ml. of acid and 100 ml. of water are placed in a 300-ml. conical flask in the thermostat, and in another flask 25 ml. of bromate. When the solutions have had time to acquire the temperature of the thermostat they are mixed and the time is noted. At intervals of 2, 3, 5, 7 and then by intervals of 10 minutes, 25-ml. portions of the reaction mixture are withdrawn, poured into 50 ml. of ice water (to slow the reaction), the mean time being recorded, and then titrated with thiosulphate. A second mixture is prepared in a similar way, containing 50 ml. of iodide, 200 ml. of acid, and 200 ml. of water, and to this 25 ml. of bromate are added and the reaction is followed as before by means of thiosulphate titrations. In the second case the concentration of bromate is half that in the first, the other concentrations remaining the same.

In each case plot the number of millilitres of thiosulphate against time. When the reaction is complete 25 ml. of thiosulphate will be required for 25 ml. of reaction mixture, so that from the curves we can determine the time in each case required for one-third of the iodide to be decomposed. If these times are t_1 and t_2, and since the reaction mixtures contained

	I	II
KI	0·01 gram equivalent per litre	0·01 gram equivalent per litre
$KBrO_3$	0·01 ,, ,, ,, ,,	0·005 ,, ,, ,, ,,
HCl	0·04 ,, ,, ,, ,,	0·04 ,, ,, ,, ,,

the products of the concentrations are as 2 : 1 ; so

$$n = 1 + \frac{\log t_1 - \log t_2}{\log 1 - \log 2}$$

A second value for n can be found by taking the times from the curves corresponding to half transformation, i.e. 12·5 ml. of thiosulphate.

Methods of determining End-point. In all kinetic measurements either the initial concentration or the final reading ($t = \infty$) must be accurately known. This can be done either directly or, where circumstances do not permit, by extrapolation. The direct method, especially for the end-point, is subject to an experimental error much greater than is desirable in a quantity which is very heavily weighted in the calculations, and extrapolation means that the reading v_∞ at $t = \infty$ will be no more accurate than any of the other readings, but will still carry exceptional weight.

These difficulties have been dealt with statistically by Guggenheim[1] and especially by Roseveare.[2] The latter recommends that if a sufficiently accurate method is available the initial concentration should be determined directly, since this procedure is subject to a smaller experimental error than the extrapolation one. Where the reading v_∞ corresponding to the end-point is not accurately known, Guggenheim suggests taking n extra readings each a fixed time τ after the first set, where τ is several times greater than the half-period of the reaction. Then it can easily be shown that

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[1] *Phil. Mag.*, 1926, *2*, 538.

[2] *J. Amer. Chem. Soc.*, 1931, *53*, 1651.

$$kt_i + ln(v_i' - v_i) = \text{a constant},$$

where v_i' is the reading at time $t_i + \tau$.
If now $\log(v_i' - v_i)$ is plotted against t, the straight line so obtained will have a gradient $-k \log e = -0{\cdot}4342k$.

This method considerably improves the accuracy of the value of k when the end-point is not accurately known.

SECTION 7: THE EQUILIBRIUM CONSTANT

If a chemical reaction in a homogeneous system, either for example in the gas phase or in dilute solution, can be represented by the equation

$$m.\mathrm{A} + n.\mathrm{B}. \rightleftharpoons p.\mathrm{C} + q.\mathrm{D} \quad . \quad . \quad . \quad . \quad (1)$$

when equilibrium has been reached, the law of Mass Action of Guldberg and Waage tells us that the relation

$$\frac{[\mathrm{A}]^m.[\mathrm{B}]^n}{[\mathrm{C}]^p.[\mathrm{D}]^q} = \mathrm{K}_c \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

will hold, where $[\mathrm{A}]^m$ means the concentration in gram-molecules per litre of the substance A raised to the power of m, m being the number of molecules of A which occurs in the equation representing the reaction.

K_c is called the equilibrium constant at constant volume. It is a constant which is characteristic for each reaction and which varies only with the temperature.

In the case of gas reactions it is often more convenient to use the partial pressures p_A, p_B, &c., of the various components of the system ; the equation then becomes

$$\frac{p_\mathrm{A}{}^m.p_\mathrm{B}{}^n}{p_\mathrm{C}{}^p.p_\mathrm{D}{}^q} = \mathrm{K}_p \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where K_p is the equilibrium constant at constant pressure.

The two constants are related by the equation

$$\mathrm{K}_p = \mathrm{K}_c(\mathrm{RT})^{m+n-p-q} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The Equilibrium Constant for Water Gas. A relatively simple gas reaction which can be used to test the law of mass action is that represented by the equation

$$\mathrm{H_2O} + \mathrm{CO} \rightleftharpoons \mathrm{CO_2} + \mathrm{H_2} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The equilibrium constants for this reaction are given by

$$\frac{[\mathrm{H_2O}].[\mathrm{CO}]}{[\mathrm{CO_2}].[\mathrm{H_2}]} = \mathrm{K}_c = \frac{p_{\mathrm{H_2O}}.p_{\mathrm{CO}}}{p_{\mathrm{CO_2}}.p_{\mathrm{H_2}}} = \mathrm{K}_p = \mathrm{K} \quad . \quad . \quad (6)$$

Equation (5) shows that the reaction produces no change in the total number of molecules, so that it follows from equation (4) that the equilibrium constants at constant volume and constant pressure have the same value.

The method of carrying out the experiment consists in introducing measured volumes of carbon dioxide and hydrogen into the reaction vessel, causing them to react at a certain high temperature and analysing the resulting gas mixture.

The necessary high temperature is provided by a platinum wire which can be heated to a bright red heat by means of an electric current. The hot platinum also acts as a catalyst for the reaction and hastens the attainment of equilibrium.

The reaction occurs so slowly at the room temperature that it is undetectable, but at a red heat in the presence of the platinum it proceeds with great rapidity. The products of the reaction are removed from the neighbourhood of the catalyst by their own rapid motion at the high temperature and on reaching the colder parts of the apparatus are themselves cooled so that the reaction stops. By this process the equilibrium is said to be ‘ frozen ’.

If the reaction products were cooled slowly in the neighbourhood of the catalyst a fresh equilibrium would tend to be set up at each temperature and the composition of the final mixture would be very different from that which it had at the high temperature : it is only this method of ‘ freezing the equilibrium ’ which enables us to get the values corresponding to the high temperature.

In studying any case of equilibrium in a homogeneous system it is of course necessary to ensure that none of the substances leave the system. In this case we must take particular care that none of the water produced leaves the gaseous phase, otherwise the equilibrium set up will not be the one corresponding to our measurements of the amounts of the four gases. We must avoid, therefore, the condensation of water on the walls of the reaction vessel and on the surface of any confining liquid used.

Measurement of the Equilibrium Constant for the Water Gas Reaction and to verify the Law of Mass Action. The apparatus required is shown in Fig. 13 (IX^3). F is the glass reaction vessel which has a capacity of 200 ml. The wide mouth at its lower end is closed with the large rubber stopper R and at its upper end is a narrow-bore tube with a stop-cock S. B is a gas measuring-burette with a levelling tube at the side. This burette contains a concentrated solution of common salt and can be connected to the reaction vessel by the narrow-bore tube t_2.

The lower part of the reaction vessel F is surrounded by the metal jacket M, this contains water and a thermometer T and can be heated by means of the small gas jet shown at G. t_1 is a tube which passes through the stopper R and connects the reaction flask to a levelling vessel containing paraffin oil : this oil serves as the retaining liquid for the gas in F and it is on this oil surface that we have the danger of condensation of water ; this is the reason for the hot-water jacket M. The upper glass parts of F get so hot during the glowing of the platinum wire that there is no danger of condensation there.

W is the platinum wire of length 3–4 cm. and 0·5 mm. diameter ; it is sealed into the glass tubes as shown and is joined to the thick copper leads LL. It will be necessary to maintain the wire W at the same temperature in successive experiments ; this can be done with sufficient accuracy if we keep constant the voltage across LL and the current in W ; a voltmeter (0–20) is therefore connected across LL and in series with W is an ammeter (0–20), a rheostat (2 ohms to carry 20 amps.), a battery of accumulators to give 16 volts and a key.

For the analysis of the gas mixture we require a gas absorption pipette containing 40 per cent caustic potash and a second one containing a solution of cuprous chloride in 8 per cent ammonia: the former to absorb carbon dioxide and the latter for carbon monoxide.

Method.—Before starting the experiment the water in M is heated to between 60° and 70° with F full of oil right up to the top. B is then filled with salt solution by raising the levelling tube and about 60 ml. of pure carbon dioxide are introduced. This may be obtained from a Kipp's apparatus and must be washed with water and sulphuric acid and plenty of time allowed for air to be displaced from the wash bottles and the delivery tube. The volume is read off in B at atmospheric temperature and pressure and these are recorded. The carbon dioxide is then transferred to the reaction vessel F. In a similar way about 60 ml. of purified hydrogen is added to B and the volume, temperature, and pressure again read; this gas is also transferred to the reaction vessel and the tap S is closed.

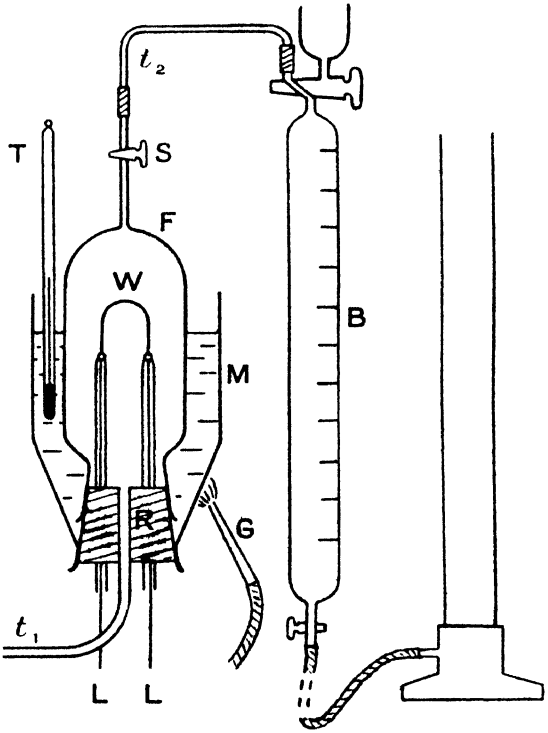

FIG. 13 (IX³)
Apparatus for the determination of the equilibrium constant for the water-gas reaction

The levelling tube is adjusted so that the whole of the platinum wire W lies above the surface of the oil. A small current is passed at first and is gradually raised until the platinum wire is at a bright red heat: this will require 10–18 amps. according to the proportion of hydrogen. This current is maintained for 10 minutes and is then cut off.

Allow the apparatus to cool down for about 10 minutes and then transfer a portion of the gas mixture to B for analysis; about 60 ml. is sufficient. After allowing a further period of 10 minutes for the gas to cool down to the room temperature, measure the volume of the gas mixture in B at atmospheric temperature and pressure. Transfer the gas to the potassium hydroxide absorption pipette and shake, return the gas to B and measure the volume. Repeat until no further diminution in volume is found. Next transfer to the cuprous chloride pipette and shake and again read the volume in B. Here again repeat till the absorption is complete.

The first decrease of volume gives the volume of carbon dioxide; the second gives that of the carbon monoxide and also (from the equation) that of the water if it were still in the state of gas at this temperature and pressure. The residual volume is that of the hydrogen. If there has been any appreciable change in the temperature during the course of the measurements each gas volume must be reduced to N.T.P.; otherwise this is not necessary, and each volume can be reduced to what fraction it is of the total volume, and this fraction will be the partial pressure in atmospheres.

Insert the values found in equation (6) and obtain a value for K.

A check can be obtained on the measurements made by measuring the volume of the residual gas in F. This enables us to calculate the volume of the final mixture less that of the water which has now all condensed. Since the volume of the initial mixture was measured, this contraction gives the volume of the water.

We have then the following checks

ml. of CO = ml. of H_2O = ml. contraction
Initial volume of H_2 − final volume of H_2 = ml. contraction = ml. H_2O
Initial volume of CO_2 − final volume of CO_2 = CO formed = ml. H_2O

Repeat the experiment once or twice with different initial volumes of carbon dioxide and hydrogen, e.g. 80 ml. of carbon dioxide and 40 ml. of hydrogen, &c.

Since the magnitude of K is constant only for a given temperature, the maximum temperature of the wire must be regulated to have the same value each time by means of the voltmeter and ammeter.

If the values of K found in the different experiments agree the equation from which K is calculated is correct and the law of mass action is verified.

CHAPTER X[3]

HYDROGENATION

SECTION 1: NOTES ON METHODS

THE term hydrogenation is generally used to include any process for the combination of hydrogen with organic substances especially in presence of a catalyst. A number of laboratory and semi-technical scale plants are described in Vol. I, Chap. VIII, Section 6.

In earlier experiments Sabatier employed a hard glass tube packed with the catalyst. Hydrogen was bubbled through the heated substance to be hydrogenated and the hydrogen with the vapours passed over the catalyst. Specially prepared pumice or kieselguhr with a nickel deposit was used as catalyst. The pumice is boiled with nitric acid, washed free from acid, and then sufficient of a saturated solution of nickel nitrate to give a catalyst of the proper nickel content added. The mass is evaporated to dryness, and then strongly heated to decompose the salt and deposit the oxide. The oxide-impregnated pumice is packed in the tube and reduced in a stream of hydrogen at 300°. The cooling takes place in an atmosphere of hydrogen. The apparatus of Lush [1] is more convenient for laboratory work. The catalyst is made from nickel turnings which have been partly oxidized and then reduced in hydrogen gas. It can be used at different temperatures and pressures. The apparatus and technique have been standardized.[2] The plant consists of a series of drawn-steel jacketed tubes. Each tube contains two catalyst cages. These cages are composed of monel or nickel gauze fitted with activated pure nickel turnings. At the end of the series of tubes is placed the substance for hydrogenation, &c., see Vol. I., p. 301.

Emmett and Skau [3] have studied the catalytic hydrogenation of benzene over various metallic catalysts. The purified hydrogen was bubbled through benzene maintained at 25·0° to produce a 7 : 1 hydrogen : benzene mixture and then over the catalyst, through the condenser, and into interchangeable receivers. Hydrogen could also be made to bypass the saturators for reducing the catalysts *in situ*.

An ice-bath was used for condensation of the products of hydrogenation. It was established that for low cyclohexane content the ratio of benzene : cyclohexane in the liquid condensate accurately reflected the gas phase ratio ; with a cyclohexane content above 10 per cent there was a slight preferential condensation of benzene at 0°. The composition of the vapour could thus be determined by a simple refractive index determination at 25° on the condensate with the help of a calibration chart of refractive indices.

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[1] *J. Soc. Chem. Ind.*, 1923, *42*, 219. See also Pelly, *ibid.*, 1927, *49*, 449.

[2] Technical Research Works, Ltd. (T.R. Co.), Milner St., London. They market both laboratory and technical models.

[3] *J. Amer. Chem. Soc.*, 1943, *65*, 1031.

Liquid Phase Hydrogenation. This procedure has largely replaced vapour phase hydrogenation. In its simplest form a calibrated hydrogen reservoir is in contact with a flask in which hydrogenation is carried out. The flask can be heated or evacuated and is so fitted that it can be agitated and, if necessary, the system placed under pressure. In this flask is placed the substance to be hydrogenated. It is dissolved or suspended in a suitable liquid together with the catalyst. The air is then removed, the flask agitated (and heated if necessary), and hydrogen admitted until the calculated amount has been utilized. The excess hydrogen is then evacuated and the mixture filtered to remove the catalyst.

Measurement of Hydrogenation Value. A convenient method of determining this constant has been worked out by Castille.[1] A 250-ml. reaction flask made of thick Pyrex glass contains in its elongated base an agitator which is constructed of platinum-iridium and built up from three horizontal perforated disks, and a fourth bottom disk which is slightly bell-shaped, and serves to project the liquid against the walls of the flask. To the top end of the shaft of the agitator is attached a small cylinder of soft iron which is arranged between the poles of an electromagnet in such a way that when the current supplied to the latter is interrupted every second (by means of a mercury contact operated by an electric pendulum), the agitator falls into the liquid, carrying with it, between its disks, the hydrogen necessary to effect reduction. About 0·1 gram of the sample is weighed into the small glass cup, which is then covered and suspended in a platinum ring 2 cm. above the surface of the liquid in the flask (see below); at the correct stage the magnet is raised, when the agitator also rises and the top disk strikes the cup and distributes the contents into the liquid. The pressure of the hydrogen is measured by means of a two-arm type of manometer, which is connected directly with the reaction vessel through the tube in which the agitator-shaft revolves. Any suitable catalyst may be used, but a suspension of 1 gram of spongy platinum in 25 ml. of glacial acetic acid is preferred, and this volume just covers the top disk of the stationary agitator. The hydrogen should be washed and dried, and clamps are provided for making the outlet of the reaction vessel airtight. Before the experiment starts, suction is applied five times, so as to remove as much air as possible from the system; the air is replaced each time by hydrogen, so that eventually a pressure of 1 atmosphere of this gas is obtained. The agitator is started and, after a few minutes, the catalyst is saturated with hydrogen, and when an equilibrium-condition has been reached the temperature and pressure noted. The sample is then added, the pressure is maintained as nearly as possible at the same value by adjustment of the levelling-tube on the manometer, and, after 15 minutes, absorption is complete. Then the hydrogenation value is given by 0·8973 multiplied by the volume of hydrogen absorbed (corrected to N.T.P.) and then divided by the weight of sample; an index of 100·8 is equivalent to an iodine value of 126·9. The method has been used by Castille[2] to examine two strongly unsaturated compounds from Boleko oil, viz. an aldehyde which, on catalytic reduction, produces *n*-decane, and a C_{20} compound which, on saturation, forms an acid $C_{20}H_{40}O_2$; the sensitiveness was found to be ± 0·5 and 0·1 per cent respectively.

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[1] *Bull. Soc. Chim. Belg.*, 1937, *46*, 6. Abstract from *Analyst*, 1937, *52*, 420.

[2] *Loc. cit.*

Quantitative Micro-hydrogenation. An apparatus of sufficient accuracy to measure the hydrogenated groupings in organic compounds has been described by Johns and Seiferle.[1] The apparatus is shown in outline in Fig. 1 (X^3). It is constructed of Pyrex glass. The dimensions of the various parts can be calculated from the scale. The ground-in plug A in the side-arm is hollow and to its base is sealed a piece of 2-mm. tubing

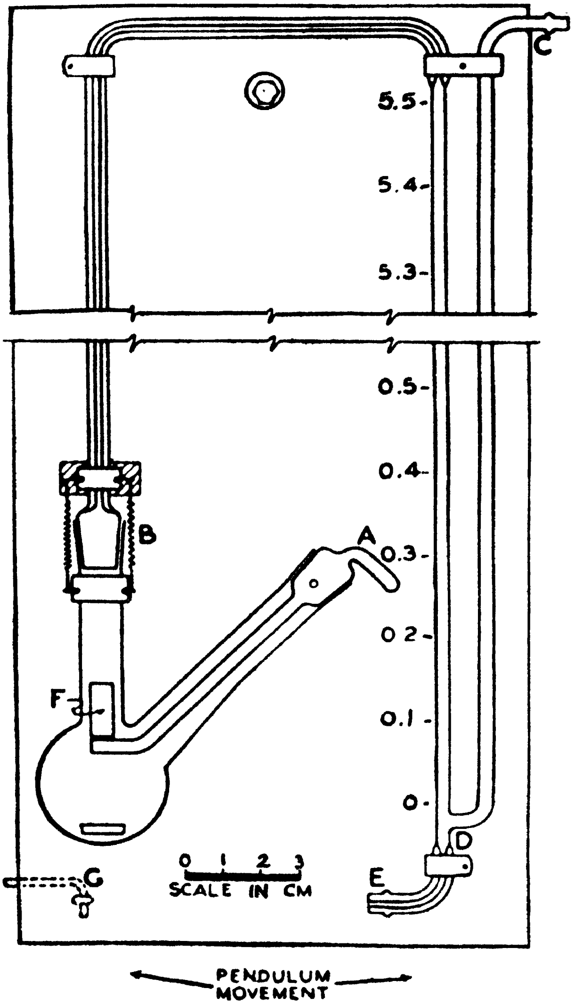

FIG. 1 (X^3)
Quantitative micro-hydrogenation apparatus

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[1] *Ind. Eng. Chem. Anal.*, 1941, *13*, 841.

which serves to retain the sample tube F in the neck of the flask until the solvent and catalyst have been saturated. Through the side of the plug and the ground surface of the side-arm are bored matching-holes about 0·5 mm. in diameter. At B is a ground-glass connexion to a capillary of 1-mm. bore which leads to the measuring-burette. It is made of tubing of uniform bore, 4 mm. in inside diameter; its capacity is about 5·5 ml. It is calibrated in 0·1 ml. divisions which can be read to ± 0·01 ml. At point D, the base of the burette, a side-tube of the same diameter as the burette is sealed. This serves both as a manometer for accurate levelling of the burette liquid and as an inlet tube, when connected at C to the source of hydrogen. A levelling-bulb is connected by rubber tubing to the apparatus at E.

The capillary above B is bent out from the board a distance sufficient to accommodate the bulb of the reaction flask, and is supported at B by being clamped to a block of wood fastened to the board. The board is pivoted and the whole apparatus is agitated by connexion to a motor-driven eccentric. A vibration rate of 200 per minute is satisfactory and a variable resistance is connected in the electrical system to control the speed of the motor.

The weighed catalyst, either Raney nickel or Adams and Shriner's platinum oxide, is introduced into the reaction flask. Then 5 ml. of solvent are added. The sample, 5 mg. or more, is weighed in a thin-walled, flat-bottomed glass capsule F. This capsule is then inserted into the neck of the reaction flask and is held in place by the end of the tube attached to the base of plug A, bent as shown. This tube must be so bent that the holes in the plug and side-arm meet sufficiently to effect an opening to the apparatus while the capsule is held in position. With A adjusted at the open position, the flask is attached to the capillary manifold through the greased connexion at B, and is held firmly in position by springs. The liquid in the burette, preferably mercury, is lowered below D and hydrogen is swept through the apparatus for several minutes, in at C and out at A. This procedure is an advantage over the method previously used, of alternately evacuating the apparatus and introducing hydrogen, repeating 6 to 10 times.

Before the hydrogen enters the apparatus it is bubbled through a tower containing alkaline stannite solution to remove traces of oxygen and then through a saturator containing the same solvent used in the reaction flask. This procedure reduces to a minimum the time necessary for saturation of the atmosphere in the apparatus. The hydrogen is led through a small-bore tube to the bottom of a side-arm test tube which is filled with glass beads covered by the solvent. It is advisable to insert a Bunsen valve in the inlet tube from the hydrogen cylinder.

When the apparatus has been thoroughly swept out the source of hydrogen is disconnected, plug A is closed, still holding capsule F in place in the neck of the flask, and the apparatus is let stand until thermal equilibrium is reached. The mercury is then raised until it is exactly at zero in the side-tube, A is opened momentarily to equalize the pressure in the apparatus and to adjust the mercury at zero in the manometer, and is then closed, still retaining the capsule in the neck of the flask. The catalyst and solvent are saturated with hydrogen, the apparatus being shaken by means of the electrically driven eccentric. Completion of saturation is attained when on continued agitation no further change in the burette reading is observed. This reading is recorded as the initial reading for the hydrogenation of the sample.

Plug A is then turned to allow capsule F to drop into the solvent, the side-opening at A being kept closed. Shaking of the apparatus is begun again and the hydrogenation proceeds. Observations of hydrogen consumption may be made at intervals, the shaking being stopped momentarily, and the final reading is made when no further consumption of hydrogen is evident. The temperature at the apparatus is read at each observation, and the barometric pressure is recorded; in hydrogenations requiring several hours the pressure is noted at least at the beginning and end of the experiment.

Corrections to be applied to the readings for changes in temperature or barometric pressure are dependent upon the free volume of the apparatus. This is determined by any convenient method. Temperature changes produce variations in both partial pressure of solvent and volume of the gaseous phase.

The following example by Johns and Seiferle[1] gives an idea of the method of working.

Fumaric acid, hydrogen number, 116. Sample, 5·302 mg. Catalyst, PtO_2, 3·112 mg. Solvent, alcohol, 5 ml. Total volume, 35·3 ml. Volume of boat and capsule, 0·4 ml.

Hydrogenation of catalyst: Initial readings, V-burette = 0; P = 741·0; t = 28·0°. Final readings, V-burette = 0·69; P = 741·3; t = 28·5°.

Hydrogenation of sample: Initial readings, V-burette = 0·69; P = 741·3; t = 28·5°. Final readings, V-burette = 2·06; P = 741·3; t = 28·3°.

Vapour pressure of alcohol, 70·2 mm. at 28°, 71·5 mm. at 28·3°, 72·5 mm. at 28·5°.

$$\text{Initial } V_{H_2} = (35{\cdot}3 - 5{\cdot}0 - 0{\cdot}4) \times \frac{273}{301} \times \frac{741 - 70{\cdot}2}{760} = 23{\cdot}94 \text{ ml.}$$

After hydrogenation of catalyst

$$V_{H_2} = (35{\cdot}3 - 5{\cdot}0 - 0{\cdot}4 - 0{\cdot}69) \times \frac{273}{301{\cdot}5} \times \frac{741{\cdot}3 - 72{\cdot}5}{760} = 23{\cdot}27 \text{ ml.}$$

$$\text{Observed } V_{H_2} \text{ used by catalyst} = 23{\cdot}94 - 23{\cdot}27 = 0{\cdot}67 \text{ ml.}$$

$$\text{Calculated } V_{H_2} \text{ used by catalyst} = \frac{3{\cdot}112}{227} \times 2 \times 22{\cdot}4 = 0{\cdot}61 \text{ ml.}$$

After hydrogenation of sample

$$V_{H_2} = (35{\cdot}3 - 5{\cdot}0 - 0{\cdot}4 - 2{\cdot}06) \times \frac{273}{301{\cdot}3} \times \frac{741{\cdot}3 - 71{\cdot}5}{760} = 22{\cdot}23 \text{ ml}$$

$$V_{H_2} \text{ used by sample} = 23{\cdot}27 - 22{\cdot}23 = 1{\cdot}04 \text{ ml.}$$

$$\text{Hydrogen number} = \frac{5{\cdot}302}{1{\cdot}04} \times 22{\cdot}4 = 114$$

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[1] *Loc. cit.*

It is unnecessary to calculate the volume of hydrogen used by the catalyst. It is shown here in calculation to indicate the close agreement between the observed volume and the volume calculated from the weight of platinum oxide employed. Catalyst and sample can be hydrogenated simultaneously, correcting the hydrogen utilized by subtracting the calculated volume of hydrogen used by the catalyst.

Hydrogenation at High Pressure. For hydrogenation of small quantities of material at high pressure the technique of Gibson and Baskervilles [1] can be employed. The procedure is as follows. The material to be hydrogenated, together with catalyst, and solvent (if used), is placed in the reaction vessel whilst it is open and supported in the heater. The cover complete with agitator is then placed in position, the nut lifted on and screwed down by hand as far as it will go and the six compression screws tightened down evenly. Very little tightening is required to make this joint. A thermocouple is next inserted in the thermocouple pocket, the solenoid is lifted into position and this latter connected to the valve and pressure gauge assembly by means of a connecting-tube. The apparatus is now ready for evacuation and filling with hydrogen.

With the proper valves open and the hydrogen cylinder valves closed, the apparatus is evacuated by means of a rotary oil pump. When the desired vacuum is attained, one valve is closed and hydrogen is admitted direct from the cylinder, by way of the second valve, until the required initial pressure is reached. The second valve is then closed and as a routine measure a leak test is carried out by allowing the apparatus to stand for an interval of 5 to 10 minutes. During the first minute or two of this interval a slight pressure drop always occurs, but afterwards, if the apparatus is pressure-tight, there is no further change. The gauge reading is then noted and the heater turned on. Agitation is commenced by switching on the solenoid current and setting the contactor pendulum in motion; the degree of agitation being varied, as previously described, until it is considered satisfactory. After a little experience this can easily be judged from the sound made by the agitator as it moves up and down inside the autoclave.

By previous calibration the volume of the autoclave is known and the hydrogen absorption corresponding to any observed drop in pressure can be readily calculated; due allowance being made, of course, for the volume taken up by material in the vessel, and vapour pressure and temperature factors. With the 300-atmosphere gauge, the pressure drop can be determined to within 2 atmospheres and with the 20-atmosphere gauge, to within one-sixth of an atmosphere. When dealing with 400 ml. of material in the vessel, the pressure drop per mole of hydrogen absorbed approximates to 22 atmospheres.

When a reaction is completed and the autoclave has cooled to room temperature, it is opened up, the procedure being the reverse of that already described for starting. The main joint between the cover and the vessel is, however, so well made each time that it is desirable to break it carefully in order to preserve the joint ring. This is accomplished by means of a simple device. Two set screws passing through a split ring which can be clamped to the cover are screwed against a flat ring, temporarily located on the threaded part of the vessel, thereby levering off the cover evenly and easily.

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[1] *Chemistry and Industry*, 1943, LXII, 450, see also Vol. 2, chapter on high-pressure technique.

Catalysts. Substances other than platinic oxide are also employed in various processes. Platinum black, colloidal platinum and palladium with various forms are often used. Nickel in the form known as Raney nickel is especially useful.[1, 2] It is prepared by the action of sodium hydroxide solution on an alloy of nickel and aluminium having the composition Al_2Ni. 300 grams of the finely ground nickel-aluminium alloy are added slowly (2 or 3 hours) to a solution of 300 grams of sodium hydroxide (80 per cent) in 1,200 ml. of distilled water, contained in a 4-litre beaker surrounded by ice. The mixture is then heated on a hot-plate for 4 hours with occasional stirring at 115°–120°. A further 400 ml. of a 19 per cent solution of sodium hydroxide is added and the mixture kept at 115°–120° for about 3 hours or until bubbles of hydrogen are no longer evolved, after which it is diluted to a volume of 3 litres. The clear solution of sodium aluminate is decanted, and the nickel washed by decantation six times, and then alternately by suspension and by washing on a Buchner filter with distilled water until the filtrate was neutral to litmus. The nickel is then washed three times with 95 per cent ethanol and kept under ethanol in glass-stoppered bottles. Nickel prepared by this process is so reactive that it deoxygenates nitrobenzene, *o*- and *p*-nitrobenzene and *p*-nitrophenol with 38 to 50 per cent yields of azo- and azoxybenzenes, when mixed with the nitro compounds in an open beaker.

The outstanding characteristic of the Raney catalyst is its activity at low temperatures and pressures. For example, according to Covert and Adkins,[3] with a supported nickel catalyst, acetone did not undergo hydrogenation in any considerable amount much below 100°, while with the Raney catalyst, complete hydrogenation was obtained after 11·2 hours at 23° and 2 to 3 atmospheres' pressure. Similar hydrogenations were obtained with mesityl oxide and acetoacetic ester. Complete hydrogenations at room temperature but at 110 atmospheres' pressure were obtained with benzaldehyde, acetaldehyde, cinnamaldehyde, azobenzene, and benzyl cyanide. In the case of all of these compounds, hydrogenation proceeded to completion at pressures and (or) temperatures below those at which the supported catalyst was sufficiently active for the satisfactory hydrogenation of these compounds. Both catalysts are active against certain alkenes such as styrene at 23° and 2–5 atmospheres. The hydrogenation of aldol, furfural, and the diethyl furfural acetal also proceeded at temperatures somewhat lower than have been observed with the supported catalyst. In the case of benzene, toluene, acetophenone, benzyl alcohol, ethylbenzoate, diethyl phthalate, and pyridine the Raney catalyst was not active at markedly lower temperatures and pressures than was the supported catalyst. (The ratio of nickel to organic compound in the experiments referred to in this paragraph was in most instances approximately 1 to 15.)

Other forms of nickel catalyst are also employed, e.g. Sully [4] makes an

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[1] Covert and Adkins, *J. Amer. Chem. Soc.*, 1932, *54*, 416.

[2] U.S.A. Patent 1628190.

[3] *Loc. cit.*

[4] *Chem. and Ind.*, 1939, *58*, 282.

active catalyst by precipitating nickel carbonate from nickel sulphate by means of sodium carbonate. The precipitate is thoroughly washed and reduced in a current of hydrogen.

In connexion with the general subject of high-pressure technique discussed in Vol. I, several references to high-pressure hydrogenation are given. In particular

(i) an apparatus for small-scale continuous hydrogenation is given in Fig. 21 (IX), p. 343.

(ii) a catalytic vessel designed for the study of the reaction between hydrogen and carbon monoxide in the formation of organic substances is shown in Fig. 22 (IX), p. 344.

(iii) For pressures up to 12,000 atmospheres the apparatus in Fig. 23 (IX) has been employed.

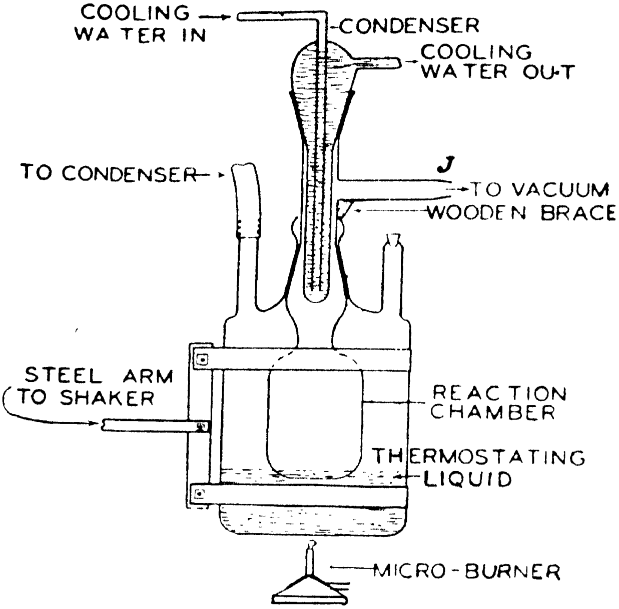

FIG. 2 (X^3)

Calvin's hydrogen absorption apparatus

Homogeneous Catalytic Hydrogenation. Quinone in quinoline solution has been hydrogenated by Calvin[1] using dissolved cuprous acetate as the homogeneous catalyst. He has shown that probably a dimer of a cuprous acetate-quinoline complex is responsible for the activation of the molecular hydrogen. The experiment consisted in following the rate at which hydrogen was absorbed by a given solution varying the concentration, solvent, temperature, and reactants. The details[2] of the vessel are shown in Fig. 2 (X^3). The internal condenser was removed and weighed amounts of the catalyst and substrate introduced. The vessel was then mounted in the shaker and connected to the vacuum system through the ground joint J. The solvent was run in from a pipette and the condenser quickly replaced and the tap to the vacuum system opened. Before air could be removed, some oxidation had taken place, so that blank runs without substrate were made on a given catalyst to determine the correction to be applied to the amount of hydrogen absorbed. The heating was then commenced and pumping was continued until the McLeod gauge at the other end of the system showed a pressure of 10^{-4} mm. or less. This degassing sometimes took as long as 30 minutes after the thermostat liquid had reached its boiling-point. For runs at 100° water was used and for 117·7° *n*-butyl alcohol was used as thermostat liquid. In all the runs the shaker speed was approximately 325 vibrations per minute. In the course of one run the shaker speed was increased to 530 vibrations per minute for a time and then decreased to 325 again and no appreciable break in the rate curve was observed, showing that the rate of solution of the gas was sufficiently fast not to be a disturbing factor.

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[1] Calvin, *Trans. Faraday Soc.*, 1938, *34*, 1181.

[2] *J. Amer. Chem. Soc.*, 1939, *61*, 2230.

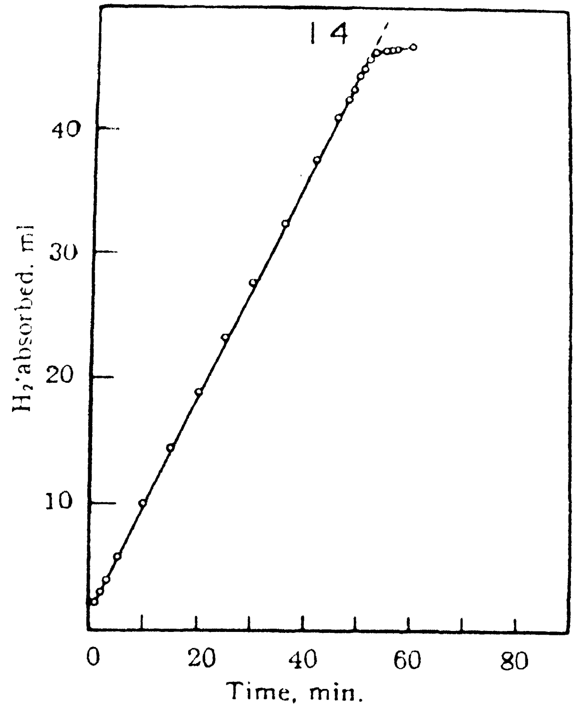

FIG. 3 (X^3)

Relation between hydrogen absorption and time in a typical experiment in the Calvin apparatus

A typical run is shown in Fig. 3 (X^3). The effect in pure quinoline solution, of variation of concentration of catalyst, substrate, and hydrogen have also been investigated.[1]

The Heat of Hydrogenation. The heat of catalytic hydrogenation has been extensively studied by Kistiakowsky and his co-workers,[1] by a calorimetric method. Since the heat of hydrogenation is a much smaller quantity than the heat of combustion, more accurate values for the differences in heat contents of organic bodies can be obtained. The method complements combustion measurements. For theoretical deduction from this extensive study, the original papers should be consulted. A description of the method for the study of catalytic hydrogenation only will be described here.

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[1] *Loc cit.*

A constant stream of the reactant gases is passed over a catalyst contained in an adiabatic calorimeter, and the products are discharged as waste until the calorimeter has reached a state of steady change, and the time-temperature relationship has become linear. A short time later, without disturbing in any way the flow, the effluent gases are directed to the measuring-unit, and the temperature of the calorimeter is noted at the instant of change. During the ensuing interval the quantity of gases which pass through the calorimeter is measured. After the desired temperature rise in the calorimeter has occurred, the gas flow is changed instantaneously from the measuring-device to waste and the temperature of the calorimeter is again noted. These operations give the temperature rise caused by the heat evolved from the measured quantity of reacting gases. The electrical energy equivalent of the calorimeter is obtained by supplying electrical energy at a constant rate and determining the rate of temperature change. This is done by measuring the temperature rise for an arbitrary time interval during which the time-temperature relationship is linear, and for which the total energy input is known. From these data, after a correction has been applied, the heat of the action can be calculated. A method of this type probably is not capable of being developed to such high precision as the standard calorimetric procedure. However, results have been obtained which are precise to nearly 0·1 per cent.

Kistiakowsky's calorimeter consists of a gold-plated cylindrical copper vessel of 1·5 litres capacity with a tightly fitting cover. It is suspended in a gold-plated calorimeter jacket of the Richards ' submarine ' design by three thin rods of low-conductivity chrome-nickel steel which provide a rigid mount; the interspace is about 3 cm. wide on all sides. The calorimeter contains a central propeller-stirrer driven by a synchronous motor through a positive drive; a glass reaction-vessel, containing the catalyst; an electric heater; and two multiple junction thermocouples, denoted in the following as thermals. The reaction vessel (see Fig. 4 (X^3)) of elongated annular shape, is followed by a glass spiral containing 2 metres of 5-mm. tubing, through which the gases must pass before leaving the calorimeter. It consists of A, annular catalyst chamber; B, platinum gauze ring to support the catalyst; C, two concentric glass spirals.

The apparatus, including the calorimeter and a reference temperature bath, is mounted within a large air thermostat maintained steady to ± 0·1°, just below the working range of the calorimeter.

The gas to be hydrogenated, e.g. ethylene, after passing a reduction gauge, flows through an automatic flow-regulating device capable of maintaining the rate constant even though the back pressure may be changing slowly. This device was found necessary as the reduction gauges were inadequate to maintain the flow to the constancy desired. Small variations in the flow of hydrogen, which is present in excess, are immaterial and thus a reduction gauge is sufficient. Ethylene passes a flowmeter, a tube filled with the catalyst, and is then mixed with the hydrogen. Both gases flow through a glass spiral 2 metres long immersed in the calorimeter bath to be heated to the temperature of the calorimeter before entering it. Hydrogenation occurs on about 100 grams of copper catalyst prepared by reduction of Kahlbaum copper oxide, analytical grade, in hydrogen at 180°–200°. After reduction, the copper is not brought into contact with the air. This catalyst is sufficiently active to hydrogenate 50 ml. or more of ethylene per minute even at 0° to the extent of 99 per cent or more. Various catalysts have been used by Kistiakowsky; these include cobalt, nickel and a 10 per cent platinum on asbestos. The latter was used for experiments on the hydrogenation of acetylene and methyl acetylene. The original papers[1] should be consulted for details.

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[1] *J. Amer. Chem. Soc.*, 1935, *57*, 65, 876; 1936, *58*, 137, 146; 1937, *59*, 831; 1938, *60*, 440, 2764; 1939, *61*, 1868, &c.

After leaving the calorimeter, the gases pass through a special double needle valve, a half-turn of the handle sufficing to send the stream either to the outside or into the gas-measuring system. The flow of the gases is not interfered with in the instant of turning and flow resistances are balanced in both paths of the gases. At the instant of turning the valve an electric contact automatically sends a signal to the same tape on which is recorded the time and the temperature of the calorimeter. Suitable devices provide that even should the needle valve leak, no loss of gas from the measuring system occurs during the run and none enters it during the fore- and the after-periods.

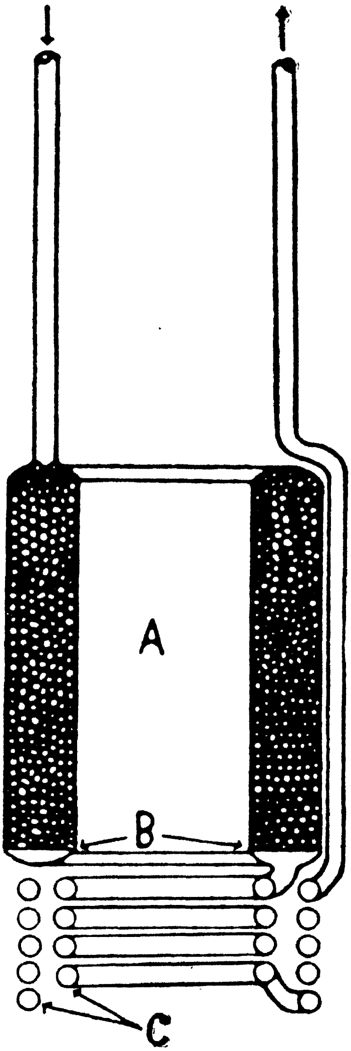

FIG. 4 (X^3)
Reaction vessel of Kistiakowsky's apparatus

During the fore-period in each chemical run a sample of the effluent gases is collected in a 1-litre flask for a test of the completeness of the reaction. The analytical method devised is capable of detecting fairly accurately as little as 0·1 ml. of ethylene in 1 litre of hydrogen-ethane mixture.

Hydrogenation with Thermal Decomposition. The process consists in decomposing an organic substance in a current of hydrogen and passing the resulting products over a catalyst. Under controlled conditions the oxygen of the original substance can be quantitatively recovered as water, the nitrogen as ammonia, sulphur as sulphuretted hydrogen, and halogens as the corresponding acids. The method was originally worked out by Meulen.[1] Its most important application is in the estimation of oxygen.

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[1] *Loc. cit.*

Much work has been done using this technique, e.g. heating the substance under test in a stream of pure hydrogen gas and allowing the resulting gases to pass over a catalyst. The water formed can be collected and weighed. A good account of the present position with many references is given by Goldsmith in *Thorpe's Dictionary of Applied Chemistry.*[2]

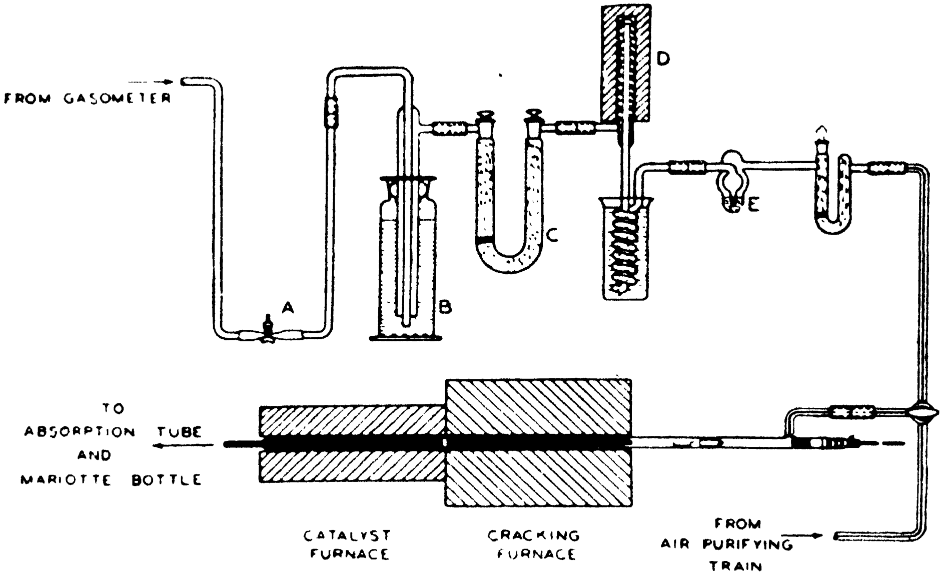

FIG. 5 (X[3])
Kirner's apparatus for hydrogenation with thermal decomposition

The best catalysts appear to be nickel chromate and nickel-thoria. These are unaffected by sulphur. With modification by cracking over platinized silica before hydrogenation these catalysts can also be used for halogens[3] and the halogen compounds separated by passing over heated silver and lime. The water formed can be absorbed in naphthyl-phosphoryl[4] or in cinnamoyl chloride[5] and the liberated hydrogen chloride titrated. Kirner[6] absorbs the water in anhydrous calcium sulphate. A further reference may be given to his apparatus based on that of Meulen's hydrogenation process as typical for such work.

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[1] *Rev. trav. Chim.*, 1922, *41*, 112, 509; 1924, *43*, 899; *Bull. Soc. Chem.*, 1931, *49*, 1098; *Chem. Weekblad*, 1936, *33*, 248.

[2] 1943, *6*, 359; Longmans, Green & Co., London.

[3] Interzaucher and Bürger, *Ber.*, 1937, *70*, 1392; 1938, *71*, 429.

[4] Lindner and Wirch, *Ibid.*, 1937, *70*, 1035.

[5] Lacourt, *Bull. Soc. Chim. Allg.*, 1937, *46*, 428.

[6] *Ind. Eng. Chem. Anal.*, 1937, *9*, 535.

Kirner's apparatus is shown in Fig. 5 (X³). Electrolytic hydrogen, taken from a high-pressure cylinder, was transferred to a large gasometer and stored over distilled water. The hydrogen passed from the gasometer through a Pregl precision screw clamp A to a Pregl pressure regulator B; the gas emerged under a pressure corresponding to about a 10-cm. column of water. From here the gas passed through a large glass-stoppered U-tube C, containing first an equal mixture of soda lime and Ascarite (8- to 20-mesh anhydrous calcium sulphate). The gas then entered a preheater D, which contained platinized asbestos heated to about 400° by means of an electrical heater. The gas was cooled by passage through the immersed glass spiral, entered the bubble counter E containing 50 per cent. potassium hydroxide solution, and then passed into the small U-tube, filled just like the large one, and through the three-way stop-cock and into the side-arm of the hydrogenation tube. All rubber connexions in the purifying train were made with paraffin-impregnated tubing. After passing through the hydrogenation tube, the gas entered a Pregl micro-absorption tube filled with Drierite, thence into a protection-tube, similarly filled, and then into the Mariotte bottle.

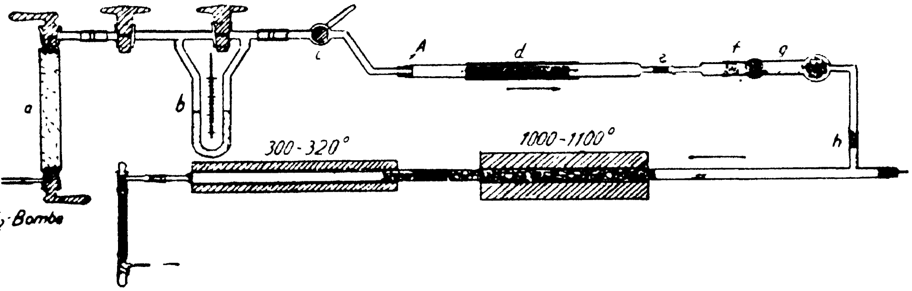

FIG. 6 (X³)
Apparatus of Unterzaucher and Bürger for hydrogenation with thermal decomposition

The quartz hydrogenation tube was 65 cm. long and had an internal diameter of 8 mm. and 1-mm. wall. To the exit end was sealed a 1-mm. capillary, 3 cm. long. The portion of the hydrogenation tube adjacent to the exit capillary, and with only the capillary protruding, was heated with a small electrical nichrome-wound furnace (catalyst furnace) 18 cm. long and 7·5 cm. in diameter. Directly against this was a second, similarly constructed high-temperature furnace (cracking furnace) 18 cm. long and 12 cm. in diameter. The catalyst furnace surrounded the portion of the hydrogenation tube which contained the "methanation" catalyst, while the cracking furnace heated that part of the tube which contained the cracking catalyst. The furnaces were calibrated throughout their entire length using a chromel-alumel thermocouple and the temperatures related to readings made on a pair of ammeters. By means of slide-wire resistances the furnaces could be adjusted to any desired temperature. The samples were weighed into platinum micro-boats and were heated by means of a bunsen burner and wire gauze roll just as in a Pregl carbon-hydrogen determination.

Unterzaucher and Bürger[1] vaporize the organic substance (3–6 mg.) in a stream of dry hydrogen. The decomposition takes place over platinized quartz followed by nickel gauze and activated nickel in quartz. The absorption of the water and not of the ammonia takes place in anhydrous calcium oxide. The apparatus is shown in Fig. 6 (X^3). The notation on the diagram is as follows: *a* and *g* are P_2O_5-pumice driers; *b* is a pressure regulator; *c* a stop-cock; *d* a copper spiral (600°); *e*, *f*, and *h* are ground-glass joints. The reduction of the catalyst takes about 7 hours and this is followed by a blank experiment. The quartz tube is 66 cm. long and contains a silver-wool plug. The boat is 16 cm. long. The catalyst for the decomposition consists of layers of granular calcium oxide (3 cm.), nickel spiral (3 cm.), hydrogenation catalyst (18 cm.). Each layer is separated by a silver plug. The absorption vessels[2] are shown in more detail in Fig. 7 (X^3); *a* consists of ground-glass joints; *b* and *b′* movable ground-glass stoppers with groove; *c* and *c′* glass wool; *d* absorption material.

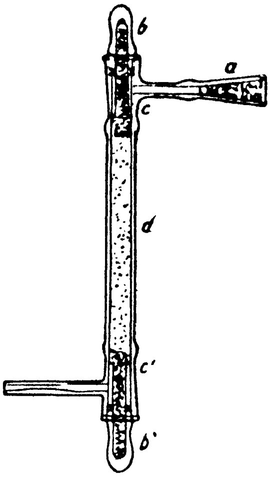

FIG. 7 (X^3)
Absorption vessel for collection of products of hydrogenation and thermal decomposition

Meulen and Ravenswaay[3] used thermal decomposition combined with hydrogenation to determine the nitrogen content of betaine, pyramidone, and sulphanilic acid. Previously Gauduchon[4] had found that with betaine hydrochloride the method gave difficulties. Meulen found that too rapid heating is a frequent source of error but, since Gauduchon found a low figure (8·27 per cent) for nitrogen in betaine hydrochloride by the Kjeldahl process (Lauro technique), it must be concluded that her sample was impure, especially as the authors obtained 9·00 to 9·02 per cent with pure samples. Gauduchon used pure nickel as catalyst; it has been shown by Meulen,[5] that nickel containing 10 per cent of thorium oxide is a more efficient catalyst. In applying the hydrogenation process to compounds containing a halogen element, it is advisable to introduce a little soda lime into the quartz tube containing the catalyst[6] in order to prevent de-sensitization of the catalyst by the halogen element.

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[1] *Ber.*, 1938, *71*, 429.

[2] Flaschenträger, *Z. angew Chem.*, 1926, *39*, 717.

[3] *Rec. Trav. Chim. Pays-Bas*, 1937, *56*, 1022. Abstract from *Analyst*, 1937, *62*, 894.

[4] *Contribution à l'Étude de la Méthode de Kjeldahl*, Paris, 1936.

[5] *Rec. Trav. Chim. Pays-Bas*, 1934, *53*, 118.

[6] Meulen and Ravenswaay, *Chem. Weekblad*, 1936, *33*, 248.

CHAPTER XI^3

SURFACE TENSION

SECTION I: METHODS

THE general subject of surface reactions and monomolecular films have been reviewed in Vol. I, Chap. XII, Sections 5 and 6. Additional observations are recorded here.

The Differential Capillary Rise Method is due to Richards, Speyer, and Carver;[1] a form of apparatus used by Neros and Eversole[2] is shown in Fig. 1 (XI^3). Here A is the narrow capillary and B the broad one and these were examined for uniformity of bore by the usual method of measuring the lengths of a small thread of mercury at different points along the tube and for circular cross-section by a microscopic examination of the ends. The capillaries are bent as shown in the figure so that, with the apparatus upright, the surface in the wider tube lies vertically below that in the narrow one. A further precaution to avoid any error due to the deviation of the narrow capillary from a right circular cylinder was always to bring the liquid surface to the same point in this tube. A mark was etched on this tube at the point G just above the elbow: in carrying out a determination, sufficient liquid was put into the apparatus so that, when each tube was wet above the meniscus, this in the narrow tube was just below the mark G. The level of this meniscus can then be moved on to the mark by moving the glass rod D down or up by means of the screw E moving in the head of the stopper. This device makes it possible to get the meniscus at G within 0·002 cm.; of course, any error of this kind remains in the tube B but is of less importance in the wider tube. Richards's paper[3] gives full particulars of the method to be used in the measurement of the radius of the capillaries. The surface tension is calculated from the equation

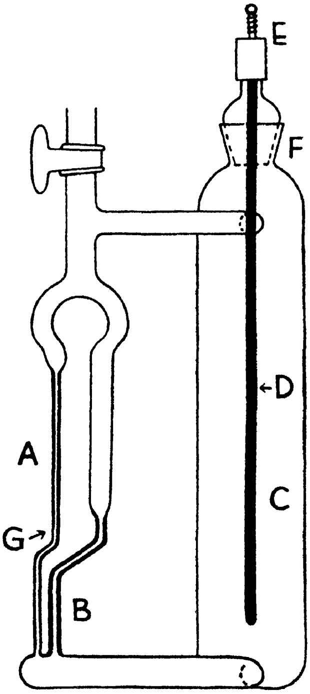

FIG. 1 (XI^3)
Surface tension by differential capillary rise method (apparatus of Neros and Eversole)

$$\sigma = \mathrm{KH}\,(\mathrm{D} - d)$$

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[1] *J. Amer. Chem. Soc.*, 1924, *46*, 1196.

[2] *J. Phys. Chem.*, 1941, *45*, 388.

[3] *Loc. cit.*

where

$$K = \frac{r_1 g}{2(1 - G)}$$

r_1 is the radius of the small tube
r_2 is the radius of the larger tube
G is the ratio r_1/r_2
g is the acceleration due to gravity
D is the density of the liquid
d is the density of the air
h_1 is the corrected height in the small tube
h_2 is the corrected height in the large tube

and $H = h_1 - h_2$, where h_1 is the corrected rise in the small tube and h_2 the corrected rise in the large tube, using the corrections due to Poisson and Lord Rayleigh.

If $h - h'$ is the observed difference in height in the two capillaries,

$$H = (h - h') + \frac{r_1 - r_2}{3} - 0{\cdot}1288\left[\frac{r_1^2}{h} - \frac{r_2^2}{h'}\right] + 0{\cdot}1312\left[\frac{r_1^3}{h^2} - \frac{r_2^3}{h'^2}\right]$$

K is a constant for any given piece of apparatus at a given temperature K has a temperature coefficient less than 1 in 1,000 over a temperature interval of 60°.

In measuring the surface tension of solutions these were allowed to stand overnight to allow capillary active impurities to rise to the surface and the liquid to be used was siphoned from below.

Another form of apparatus using Richards's differential method is that shown in Fig. 2 (XI^3), which is due to Eversole, Wagner, and Bailey.[1] Here the apparatus includes means for measuring the vapour density and the specific gravity of the liquid. The two capillary tubes are mounted side by side, but one slightly behind the other, so that both the capillaries may be in the field of view of the measuring-microscope and either may be viewed by making a small change of focus. At F is shown a calibrated quartz spiral with a hollow quartz bob at G. The spiral is suspended from the glass loop C by means of the platinum hook D and the platinum hook E. This part of the apparatus was inserted through the bottom of the wide tube on the right and assembled before this tube was sealed. The side-tube is for the addition of the liquid and after evacuation of air is sealed off. When in use the apparatus is placed in a thermostat in the position shown and readings of the capillaries give the surface tension and of the spiral the density of the vapour. The apparatus

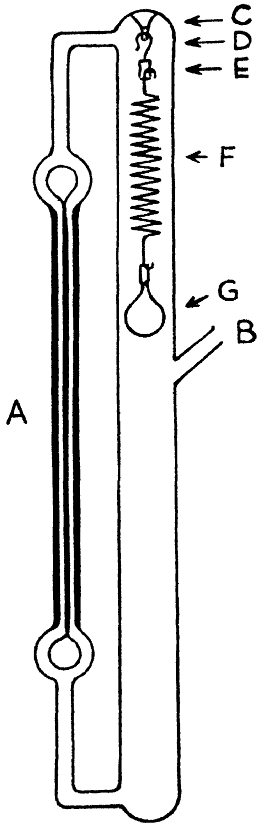

FIG. 2 (XI^3)
Surface tension differential method of Richards

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[1] *J. Phys. Chem.*, **1941**, *45*, **1390**.

is then inverted and a second value of the surface tension is obtained, while the reading of the spiral in this position gives the specific gravity of the liquid.

Calibration was carried out using chloroform as the standard liquid, the mid-part of A being the place to which the menisci were brought in either position by the use of a suitable quantity of the liquid. A correction for the rise in the large tube was made by the method described by Richards. The spiral can be calibrated by measuring its length *in vacuo*, then in the chloroform vapour and finally in the liquid ; its length is thus known under three known forces.

Method for Small Quantities of Liquid. Ferguson[1] describes a method for the determination which only requires sufficient liquid to fill a short capillary. Fig. 3 (XI³) shows the arrangement of the apparatus. A horizontal thick-walled capillary tube is used—this is shown on an enlarged scale on the left side of the diagram. The end of the tube is ground flat to a matt surface and the drop of liquid is introduced into this tube after the usual precautions as to cleaning. The pressure on the right end of the liquid column can be varied by altering the height of the pressure-regulating bottle on the right and the pressure is measured by the manometer. When the pressure is raised the liquid is forced to the left end of the capillary and the left end meniscus of the liquid column becomes in turn concave, plane, and convex. The pressure has to be raised until this surface becomes exactly plane ; the pressures on the inside and outside of the liquid are then equal, so that the pressure inside the whole of the horizontal liquid column is now atmospheric. The planeness of the surface can be judged with considerable accuracy by watching through a low-power microscope or a lens the illumination of the meniscus provided by a 6-volt lamp. The pressure inside the right-hand meniscus is now less than the pressure outside this surface by $2\gamma/R$ (provided that the angle of contact is zero) where γ is the surface tension and R the radius of the capillary tube ; this difference of pressure is also that measured by the manometer and so is equal to dgh where d is the density of the manometric liquid and h the difference of level in the two tubes. Hence $2\gamma/R = dgh$ and $\gamma = Rdgh/2$: an expression

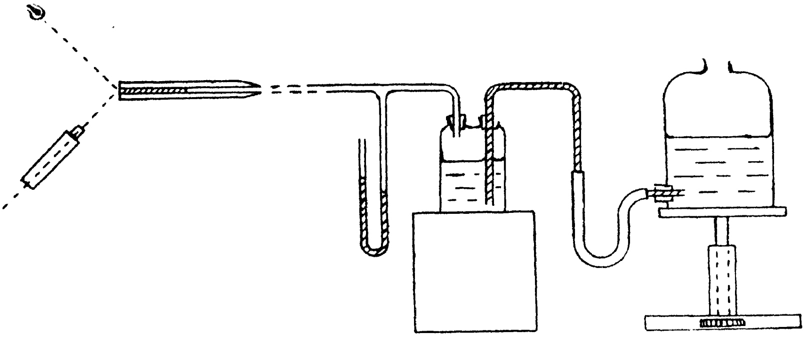

FIG. 3 (XI³)
Ferguson's micro-method for surface tension determination

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[1] *Endeavour*, **1943**, *5*, **34**.

similar to that used in the capillary rise method with the difference that the density here is that of the manometric liquid and not that of the liquid under examination.[1]

The same apparatus can be used for determinations at temperatures other than the room temperature by surrounding the central part of the capillary tube with a simple furnace consisting of a brass tube 10 cm. long and 3 cm. in diameter and overwound with nichrome wire. The capillary passes through corks which close the ends of the brass tube.

Temperatures were read with a chromel-alumel thermocouple. The arrangement is shown in Fig. 4 (XI³). For substances which were solid at the room temperature, the open end of the capillary was contained within the furnace and the corresponding end of the furnace was closed with a plate of optical glass through which the planeness of the meniscus at the end of the capillary within the furnace could conveniently be observed.

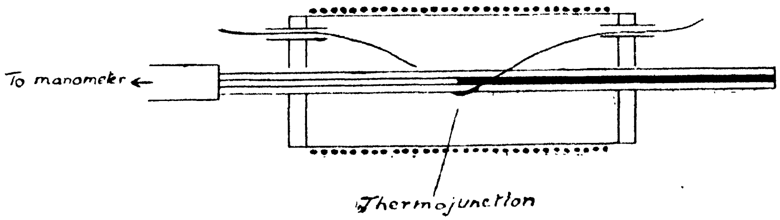

FIG. 4 (XI³)
Chromel-alumel thermocouple

As examples of the results obtainable are given figures obtained for a sample of 99·2 per cent. heavy water and for ordinary water.

HEAVY WATER		ORDINARY WATER	
t° C.	γ	t° C.	γ
12·1	72·88	17·3	72·84
15·2	72·40	20·4	72·75
20·1	71·97	25·5	71·94
24·0	71·50	28·6	71·86
30·1	70·17	30·1	71·20
35·0	69·51	34·5	70·35
39·5	68·44	38·4	70·07
45·0	67·22	44·6	68·86
50·8	66·18	50·0	68·13
55·0	65·63	60·2	65·93
61·9	64·54	65·7	65·39
64·5	63·99	73·1	63·60
69·0	63·37		
73·5	62·66		

The following is a summary of a micro-method, due to Natelson and Pearl,[2] for the determination of surface tension. The method may be followed, if necessary, employing less than 0·1 ml. of the liquid :

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[1] *Cf.* Cohan and Meyer, *J. Amer. Chem. Soc.*, 1940, *62*, 2715.
[2] *Ibid.*, 1935, *57*, 1520.

The apparatus (*see* Fig. 5 (XI³)) used with liquids of ordinary viscosities, e.g. water, acetone, consists of a capillary-tube (internal diameter 0·03 cm.) joined to a wider tube (internal diameter 0·194 cm.), the whole tube being engine-divided to read in millimetres. In a determination the tube may be used in the vertical position, in the inclined position, or in the horizontal position, the mathematical formula appropriate to the particular position being subsequently applied.

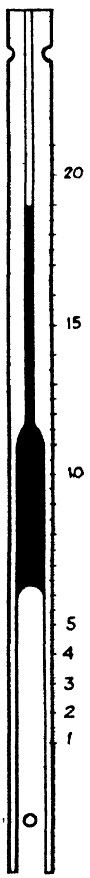

FIG. 5 (XI³)
Micro-apparatus for surface tension measurement (Natelson and Pearl)

For use in the vertical position the overall length of the tube need not exceed 15 cm. The fine capillary is touched to the liquid which is then drawn up, to a length greater than that to be used eventually, by means of an attached rubber tube. The excess liquid is then allowed to run out freely until a suitable length remains. The instrument is then inverted so that when the two menisci form, one meniscus is at a suitable position in the fine capillary and the other at a uniform part of the wider tube. The liquid is then made to run back and forth past the equilibrium positions, and then allowed to come to rest from above and from below, an interval of some minutes being allowed for the final equilibrium to be established. For ordinary liquids a 3-minute interval is found to be sufficient. Readings from above and below usually differ by a small amount. The height of the liquid is measured directly. The result is calculated from the formula:

$$\sigma = \mathrm{K}h\rho$$

assuming the angles of contact to be zero, where σ = surface tension in dynes per cm.; h = height in centimetres; ρ = density of liquid in grams per ml.; g = acceleration due to gravity; R = internal radius of wider tube in centimetres; r = internal radius of narrower tube in centimetres;

$$\mathrm{K} = \frac{g\mathrm{R}r}{2(\mathrm{R} - r)}$$

The following is a specimen result from the author's account: Water at 26° C., $\rho = 0{\cdot}997$, $h = 8{\cdot}31$, $\mathrm{K} = 8{\cdot}69$, gave $\sigma = 72{\cdot}1$ (against $\sigma = 72{\cdot}2$ by the Du Noüy Ring method).

For temperatures other than those of the room, the wider tube may be bent around so that the apparatus may be placed in a thermostat.

In using the tube in the horizontal position, the measurement of the density is avoided. The surface tension is then directly proportional to the pressure P necessary to hold the liquid stationary in both tubes, this pressure being suitably applied at the narrower end. The following formula is then used:

$$\sigma = \mathrm{P}.\frac{\mathrm{R}r}{2(\mathrm{R} - r)}$$

Addison [1] has devised an apparatus for the application of the vibrating-jet technique to the measurement of the surface tension of pure mobile liquids.

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[1] *J. Chem. Soc.*, 1943, 535.

Variation of Surface Tension with Temperature: Ferguson's equation for the variation of surface tension with absolute temperature is:

$$\sigma = \sigma_0\left(1 - \frac{T}{T_c}\right)^n$$

where T_c is the critical temperature of the liquid, and n varies in value, usually between 1·192 and 1·248, having an average value of about 1·21.

Interfacial Tension. Amongst the types of apparatus for the measurement or comparison of interfacial tensions which have been used especially in studies on emulsions (*see* Chap. XVI[3]) the following may be mentioned: (*a*) The Burette Stalagmometer (of the ordinary type when the drops sink, and fitted with a J-shaped jet when the drops rise). (*b*) The Donnan Pipette. (*c*) The Drop-Weight Volume Apparatus. (*d*) The Du Noüy Interfacial Tensiometer. (*e*) The Capillary Apparatus of Bartell and Miller.

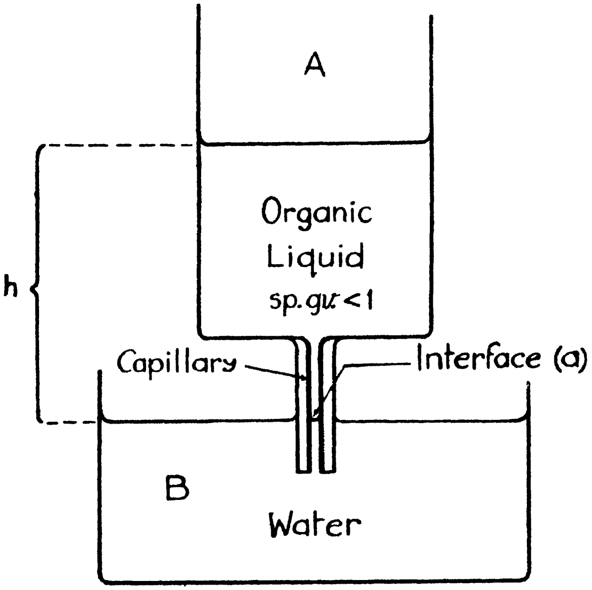

FIG. 6 (XI[3])
Interfacial tension measurement capillary apparatus of Bartell and Miller

Alexander and Teorell[1] have described a modified 'ring method'. Alexander and Schulman[2] found that in using this apparatus for low interfacial tensions, the rings need frequent cleaning as the metal rapidly turned hydrophobic. A 'drop-volume' apparatus has been described by Dedrick and Hanson,[3] and a modification of the same by Matthews.[4]

The capillary apparatus devised by Bartell and Miller[5] has been used by a number of investigators in connexion with emulsion-studies, e.g.

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[1] *Trans. Faraday Soc.*, 1939, *35*, 727.
[2] *Ibid.*, 1940, *36*, 960.
[3] *J. Phys. Chem.*, 1933, *37*, 1215.
[4] *Trans. Faraday Soc.*, 1939, *35*, 1113.
[5] *J. Amer. Chem. Soc.*, 1928, *50*, 1961.

Cheesman and King.[1] Figs. 6, 7, 8 (XI³), illustrate the forms of apparatus as originally designed.

In Fig. 6, A represents a glass cup about 4 cm. in diameter and 8 cm. deep. A capillary-tube, of about 0·3 mm. in internal radius, with a calibration mark (*a*), is sealed, as shown, to the base. B represents a wide, open dish, which eliminates effects due to capillarity. The apparatus is used as follows :

Water is placed in the dish B, and the capillary end of vessel A is immersed vertically in the water until the calibration mark (*a*) is exactly level with the external water-surface. A may then be fixed by clamping. Water rises in the capillary until the bottom of the cup A is reached ; the capillary-tube, accordingly, becomes wetted throughout its entire length. The oil (sp. gr. < 1) is then slowly added to A from a burette, the final additions being by single drops, until the interface is forced down to the calibration mark (*a*). The height, h, is then measured by means of a cathetometer, and the interfacial tension, σ_{ow}, calculated from the formula :

$$\sigma_{ow} = \frac{rhdg}{2},$$

where r = internal radius of the capillary-tube (in cm.) ; d = density of the oil ; g = acceleration due to gravity.

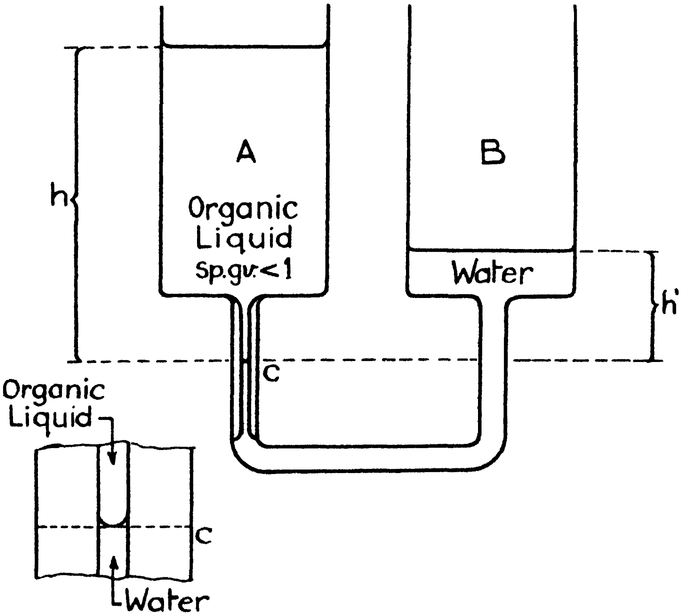

FIG. 7 (XI³)
Modified capillary apparatus

Two difficulties in connexion with the apparatus just described were pointed out by the authors, viz. that of temperature-control, and the fact that the apparatus could be used only with oils of density less than that of water. Apparatus was therefore designed by the same authors[1] to obviate these disadvantages.

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[1] *Trans. Faraday Soc.*, 1940, *36*, 241.

Fig. 7 (XI^3) represents a modified form of the apparatus. The two cups, A and B, are each similar to cup A in Fig. 6 (XI^3). They are connected by glass tubing, one arm of which consists of a capillary-tube of internal radius about 0·3 mm. In the case of oils less dense than water, about 10 ml. (or more) of water is placed in B. This water mounts the capillary-tube and completely fills the glass tubing. The oil is then added to cup A, in the same manner as previously described, until the interfacial meniscus is forced down to the calibration mark, C (*see* enlarged diagram). Heights *h* and *h'* are read by means of a cathetometer, and the interfacial tension is calculated from the formula :

$$\sigma_{ow} = \frac{rg}{2}(hd - h'd'),$$

where d' = density of water, and the other symbols have the same significance as before. The apparatus may be placed in a glass-walled thermostat,

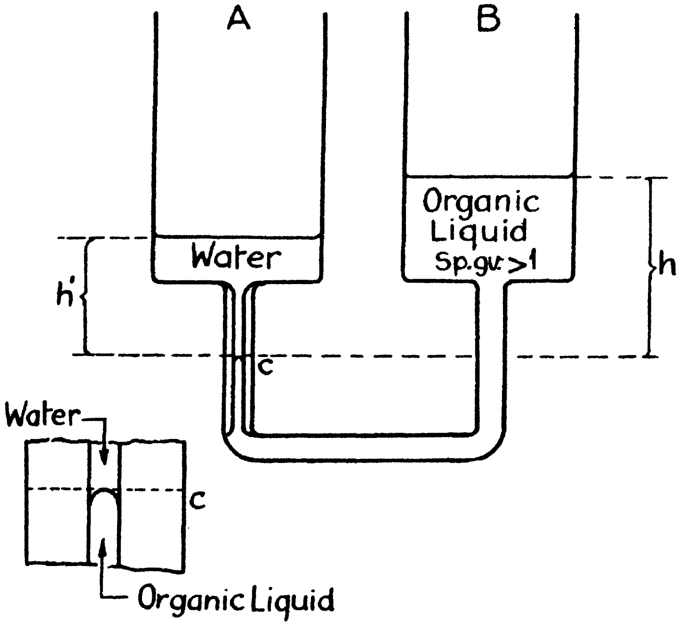

FIG. 8 (XI^3)
A second modified capillary apparatus

at the desired temperature. If the glass walls are plane, the taking of measurements, &c., will be facilitated.

If the oil be denser than water, the method of determination is modified as follows (*see* Fig. 8 (XI^3)). 10 ml. (approximately) of water is placed in A until the water rises just to the top of the tube which is attached to the base of the cup B. The oil is then added to B, in the same manner as before, until the interface just reaches the calibration mark C (*see* enlarged diagram). The heights h and h' are measured in the manner already outlined, and the formula :

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[1] *Loc. cit.*

$$\sigma_{ow} = \frac{rg}{2}(hd - h'd')$$

also applies in this case. The authors mention that Poisson's method of meniscus-correction may be applied in the case of capillaries of radius less than 1 mm.

When the quantity of oil available is limited, small-scale apparatus for the determination of the oil-water interfacial tension may be employed. Suitable types of apparatus have, for example, been designed by Mack and Bartell.[1] Fig. 9 (XI³) is a modification of a diagram, given by these authors, of an apparatus which may be used when the density of the oil is greater than that of the aqueous phase. The two cups, A and B, are each of diameter 4 cm., and of height 10 cm. The capillary-tubes sealed to the bases are of internal diameters about 0·4 mm. and 1·0 mm. respectively. These capillaries are joined at their lower ends with 5-mm. tubing, to which tubing is attached the centre tube, the upper portion of which has a diameter of 10 to 15 mm. The mouth of this centre tube is flared, as shown. The complete apparatus is made of soft glass. In a determination, water is poured into A, until both capillaries are filled. An additional 10 to 15 ml.

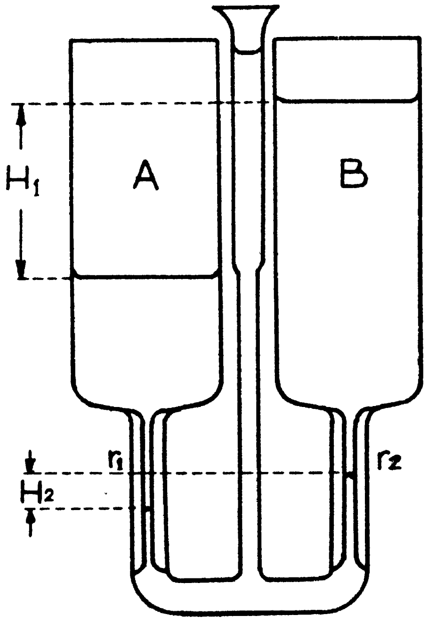

FIG. 9 (XI³)

Apparatus for the determination of the oil-water interfacial tension (density of oil > aqueous phase)

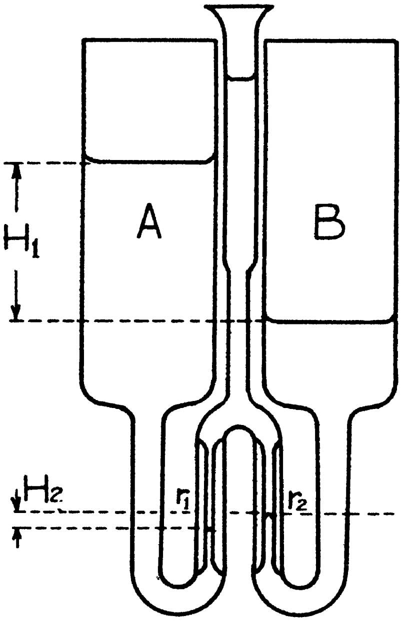

FIG. 10 (XI³)

Apparatus for the determination of the oil-water interfacial tension (density of oil < aqueous phase) of water is added to each cup, and the three levels are allowed to reach equilibrium. The oil is then added carefully through the centre tube, until the two interfaces reach the lower ends of the capillaries. The addition of the oil is then continued, drop by drop, and, at the same time, water is added to B at such a rate that the oil is prevented from running through the wider capillary. When, eventually, the oil enters the lower parts of both capillaries, the two menisci formed are adjusted, by suitable addition of liquid, so that the interface on the A side is at a slightly lower level. Oil is now added in small droplets, until the two menisci rise so as to coincide (approximately) with etched reference-marks on the capillaries. The heights H_1 and H_2 are then measured by the cathetometer, and the radius of each capillary at the position of the interface is found from calibration-curves.

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[1] *J. Amer. Chem. Soc.*, 1932, *54*, 936.

For oils less dense than water the apparatus used is indicated in Fig. 10 (XI^3). In either case, the interfacial tension, σ_{ow}, is given by :

$$\sigma_{ow} = \frac{g}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)} \{(H_1 - H_2).\rho_w + H_2\rho_o - \tfrac{1}{3}(r_2 - r_1)\Delta \},$$

where ρ_w = density of water ; ρ_o = density of the oil ; g = acceleration due to gravity ; Δ = difference between the densities of the heavier and lighter liquid. As the authors point out, the smaller the value of H_2, the less significant will the term $H_2\rho_o$ become, hence with small values of H_2 the value of ρ_o need not be determined to a high degree of precision.

The same authors[1] describe modifications of the apparatus, in which modified forms the measurement of H_1 is eliminated. The formula then simplifies to :

$$\sigma_{ow} = \frac{g}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)} \{H_2(\rho_o - \rho_w) - \tfrac{1}{3}(r_2 - r_1)\Delta \}$$

The modified types are best suited to determinations in systems where the liquids are appreciably different in density, and where such densities can be determined with high accuracy. For oils denser than water the apparatus used is indicated in Fig. 11 (XI^3), and for oils less dense than water the apparatus employed is illustrated in Fig. 12 (XI^3). The narrow capillary-tube, in either case, is about 3 cm. long, the wide capillary about 20 cm. long, and the internal radii are about the same as indicated in connexion with Fig. 9. The remainder of the tubing has a diameter of about 5 mm., the apparatus being flared at the openings. In operation, water is poured, in either case, into the right-hand tube, until both capillaries are filled. The oil is then cautiously added through the left-hand tube until the interface reaches an etched mark on the narrower capillary. The height H_2 is then measured, e.g. by means of the cathetometer. The radius of the narrower capillary at the etched mark should be known, and the radius of the wider capillary, at the level reached, may be obtained from calibration data.

Surface and Interfacial Tensions by Pendant Drop Technique. Andreas, Hauser, and Tucker[2] developed the pendant drop technique for

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[1] *Loc. cit.*

[2] *J. Phys. Chem.*, 1938, *42*, 1001.

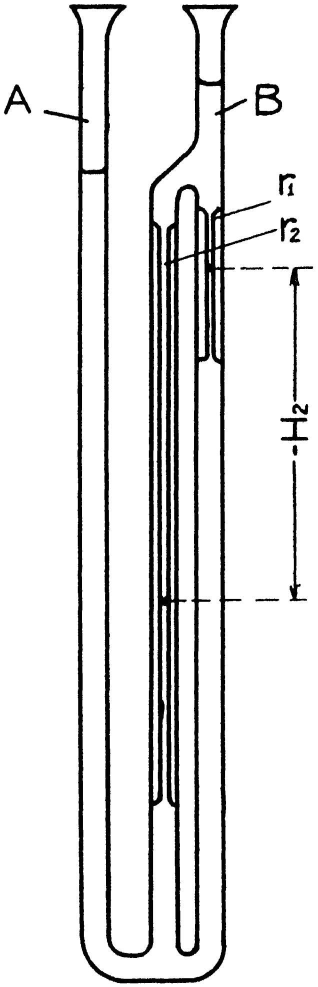

FIG. 11 (XI[3])
Modified apparatus for interfacial measurement: oils less dense than water

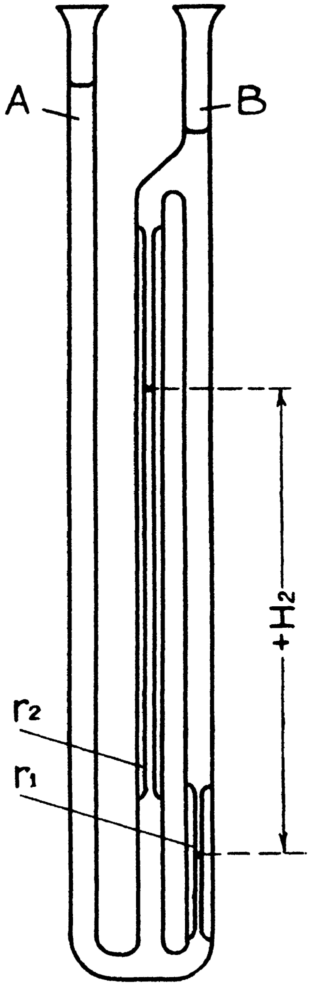

FIG. 12 (XI[3])
Modified apparatus for interfacial tension measurement: oils denser than water

the determination of boundary tension. Measurements were taken from photographic images of the drop, and the following equations were used in the calculation:

$$(a)\ r = \frac{g\sigma(d_e)^2}{H},$$

$$(b)\ H = \beta\left(\frac{d_e}{R_0}\right)^2,$$

$$(c)\ S = \frac{d_s}{d_e},$$

where r = boundary tension; g = acceleration due to gravity; σ = difference in the densities of the two fluids which form the interface; d_e =

maximum diameter of the pendant drop, i.e. the diameter at the ' equator ' ; H = a function of the drop shape ; $\beta = \frac{g\sigma R_0^2}{r}$; R_0 = radius of curvature of the drop at its vertex, i.e. at the point of intersection of the axis of rotation and the surface of the drop ; S = the ' shape factor ' ; d_s = diameter of a selected plane which cuts the drop at right angles to the axis of rotation at a distance d_e from the vertex of the drop. Values of H were determined experimentally as functions of S, and a table was published.

Other workers, also, have since designed apparatus for the application of the technique. The apparatus of Smith and Sorg [1] is illustrated in Fig. 13 (XI^3), and that of Mack, Davis, and Bartell [2] in Fig. 14 (XI^3). With reference to Fig. 13 (XI^3), the arc lamp was Type H-4 General Electric high-pressure mercury-vapour unit, and the housing contained an iris diaphragm. The green filter was a Wratten No. 62 type, the projection lens being a 400-mm. Leitz (compound). The reflex camera was a Model II Korelle-Reflex, the barrel of a Leitz microscope using a 42-mm. objective being substituted for the lens system of the camera. The camera-microscope was so mounted that by using the microscope gear-system micro-focusing adjustment was possible. The telecentric stop was a 1-mm. one. The pendant drops were suspended from 10-ml. Pyrex glass syringes with special tips of external diameters ranging from 1·25 mm. to 1·75 mm. The thermostatic water-bath was mounted on the optical bench, and it enclosed the Pyrex cuvette which was 4 cm. wide, 7 cm. high, and 2·5 cm. thick, with plane sides and a cover with a small opening to facilitate the manipulation of the syringe. The temperature in the cell-housing was maintained at 25°.

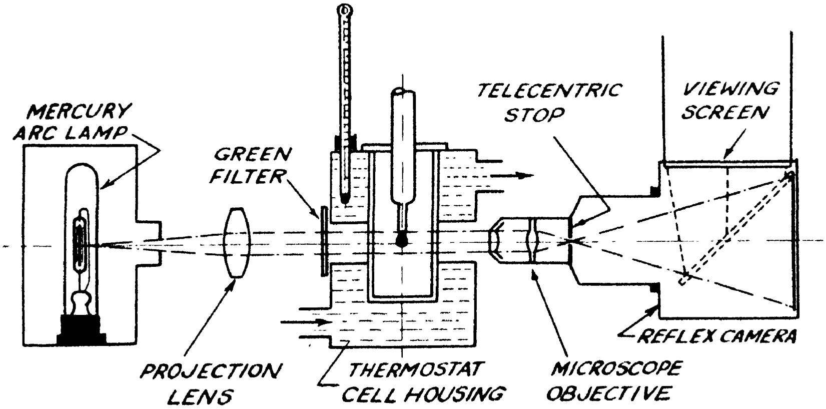

FIG. 13 (XI^3)
Boundary-tension measurement. Pendant drop apparatus of Smith and Sorg

The apparatus was used as follows : A little of the liquid was drawn into the syringe, which was then placed in such a manner that it extended well into the cuvette. A number of drops of the liquid were then expelled into the cuvette for the purpose of saturating the interior with the vapour of the liquid ; this prevented evaporation of the pendant drop at a later stage.

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[1] *J. Phys. Chem.*, 1941, *45*, 671.

[2] *Ibid.*, 1941, *45*, 846.

A pendant drop was then brought into sharp focus on the viewing-screen of the camera. When all the necessary adjustments were made, a fresh drop was suspended from the tip (to present an uncontaminated surface), and the exposure then made, the age of the drop at this stage being at most 10 seconds. The degree of magnification of the drop by the lens-system was found by photographing the rulings of a Levy-Hausser counting-chamber on each roll of film. Dimensions of drop profiles were determined from the negatives by the use of a special measuring-microscope.

The apparatus illustrated in Fig. 14 (XI^3) was used in a slightly modified form by Bartell and Davis [1] for the determination of surface and interfacial tensions by the pendant drop method. This method was found very suitable by these authors since it was necessary to prevent appreciable changes in the concentration of solute in the external phase (an aqueous solution) by extraction of the solute from it caused by the internal phase (an organic liquid). Since the relative volumes of the aqueous solution and the drop of the organic liquid were always in a ratio greater than 500 : 1, the total amount of the solute extracted by the pendant drop would be relatively insignificant, i.e. the concentration of the aqueous solution was substantially constant throughout the entire experiment. The change made in the apparatus already illustrated was that the less dense fluid (air when surface tension was measured ; the organic liquid when interfacial tension was being measured) was always the internal phase, so that the bubble (or drop) was allowed to form ‘ pendant up ’, from an ‘ inverted dropping tip ’, in the aqueous solution. In the case of the interfacial-tension measurement, it was found that after some minutes of contact between the drop and the aqueous solution a satisfactory equilibrium, enabling the completion of the experiment, was reached. Determinations were carried out at 25°.

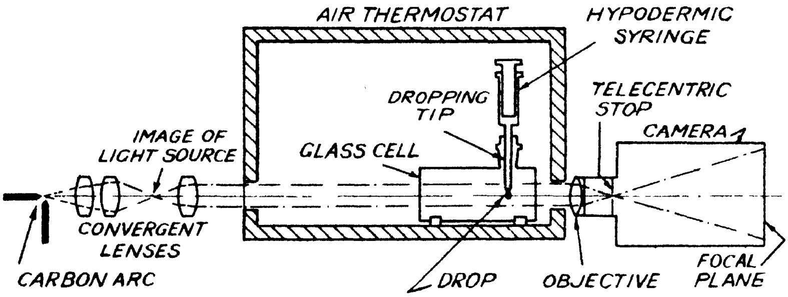

FIG. 14 (XI^3)

Boundary-tension measurement. Pendant drop apparatus of Mack, Davis, and Bartell

Monolayer Films. Phthioic acid has been found by Stenhagen [2] to form a different type of monolayer film from that of mono- or di-substituted fatty acids. Purely chemical methods have proved inconclusive in the determination of the nature of this complex branched-chain acid and so resource had to be made to such physical-chemical methods as an examination of monolayer films or X-ray reflection from crystalline layers. This second method could not be developed owing to the difficulty of obtaining suitable layers of the acid. Stenhagen[1] found that phthioic acid formed a monolayer film different in type from that of any known fatty acid, and in particular behaved quite differently from di-substituted acetic acids, e.g., decyldodecylacetic acid, collapsing at an area of about 38 Å², compared with a value of about 60 Å² and having a considerably higher surface dipole moment. Since the area of one highly compressed chain is about 18–20 Å², he concluded that the molecule contains two long chains, and postulated in addition the presence of an ethyl or methyl group in the neighbourhood of the carboxyl, which would have the effect of causing the chains to adhere more readily. Owing to the comparatively large value of the optical rotation he considered an ethyl group more likely than a methyl, and, of course, the chains must be unequal to permit of activity at all. He considered the most likely formulation to be ethyldecyldodecylacetic acid. A number of tri-substituted acetic acids and tri-substituted propionic acids have been prepared and studied by Birch and Robinson. The results are in harmony with those of Stenhagen. They are, briefly, that the films of the trialkylacetic and *βββ*-trialkylpropionic acids collapse at a much smaller area than those of the di-substituted acids, approximating to phthioic acid in their behaviour. Stenhagen obtained the collapse areas of the di-substituted acetic acids by rapidly compressing the film to a pressure of some 20 dynes, when values of about 60 Å² were found. Birch and Robinson found that the films begin to collapse at about 12 dynes, and that it was impossible to obtain reproducible curves above that pressure, the area being then about 75 Å². The tri-substituted acids, however, give definite, almost flat, collapse points, at about 11 dynes and 40 Å² in the case of the straight chain acids, and 60 Å² in the case of *β*-methyl-*β*-(*β′*-*cyclo*hexylethyl)-*β*-decylpropionic acid. Trialkylcarbinols, such as methyldioctylcarbinol, give very similar curves, but the dialkylcarbinols do not form stable films.

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[1] *Ibid.*, 1941, *45*, 1321.

[2] Quoted by Birch and Robinson, *J. Chem. Soc.*, 1942, 489.

The film measurements were made on N/100 sulphuric acid, with the type of apparatus designed by Adam, and modified by Jenkins.[2]

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[1] *Loc. cit.*

[2] *Loc. cit.*

CHAPTER XII ^{3}

VISCOSITY

SECTION 1: METHODS

(*See* Vol. I, Chap. XII, Section 7, p. 541)

A MOVING cylinder viscometer with an arrangement of coaxial cylinders with the material under test, e.g. asphalt, between them and the load applied axially to the inner cylinder was devised by Pochettino [1] many years ago for the study of high-viscosity fluids (10^{10}). This method has been restudied by Pendleton [2] for a comparison with the penetration test. A diagram of the apparatus from Pendleton's paper is shown in Fig. 1 (XII^3). The asphalt A is cast in a metal cylinder C ($2\frac{1}{2}$ in. inside diameter) with a metal rod B ($\frac{1}{2}$ in. diameter) held in place by guides (not shown) during the pouring operation. The feet D and pillars E support the cylinder C above the oven floor. The dial gauge G is rigidly fastened to C by a yoke F so that the foot H is in contact with the top of rod B throughout the test run. The rod B is loaded at I by hanging weights on an extension.

Some of the difficulties encountered in this experiment are as follows:

1. A large proportion of the total deflection was due to delayed elasticity.
2. The flow properties depended on the previous heat treatment.
3. The flow properties depended on the extent of cyclic working which breaks down the structure of the asphalt.
4. The flow properties depended on the total time of continued stress in one direction which resulted in strain hardening.

Certain elastic effects were encountered in this method which could be overcome by the penetrometer method.

The A.A.R.M. penetration test (D5-25) for comparative viscosity of viscous materials is claimed to be accurate within a small range. The standard container has a radius of 2·75 cm. and the needle 0·05 cm. The conversion of results with this apparatus into absolute viscosities has been studied. Pendleton [3] has developed the theory of the penetrometer test to a point where absolute viscosities may be determined both for viscous flow (viscosity independent of rate of shear) and generally viscous flow (viscosity dependent on rate of shear). The new penetrometer method was checked (1) with the capillary viscometer for viscous flow using coal tar pitch, and (2) with a revised axially moving cylinder method for generally viscous flow using a high-melting blown asphalt. For any one temperature, the

[1] *Nuovo Cimento*, 1914, *8*, 77.

[2] *J. App. Physics*, 1943, *14*, 171.

[3] *Loc. cit. See also* Saal and Koens, *J. Inst. Petrol. Tech.*, 1933, *19*, 176; Traxler, Pittman, and Burns, *Physics*, 1935, *6*, 58; Rhodes and Volkmann, *ibid.*, 492.

flow properties of a generally viscous material are defined by the straight line relationship between log shearing stress and log rate of shear. From this relationship viscosity may be calculated at any desired rate of shear. The slope *n* of this line is required in the calculation of rate of shear both for the penetrometer method and for any other type of standard viscometer method. An independent means for observing *n* was developed for the penetrometer and for the moving-cylinder method. It is shown that earlier formulas for standard instruments based on viscous flow are invalid when applied to fluids showing generally viscous flow properties. The power function law relating shearing stress and rate of shear has been found to hold for asphalt studied over the range of rate of shear from 10^{-5} to 10 reciprocal seconds. In addition to speed of operation and precision, the penetrometer has the advantages of minimizing the elastic effects and reproducibility without extensive heat treatment and preworking. Entire shearing stress-rate of shear curves can be determined with one load and one penetration using a succession of time intervals.

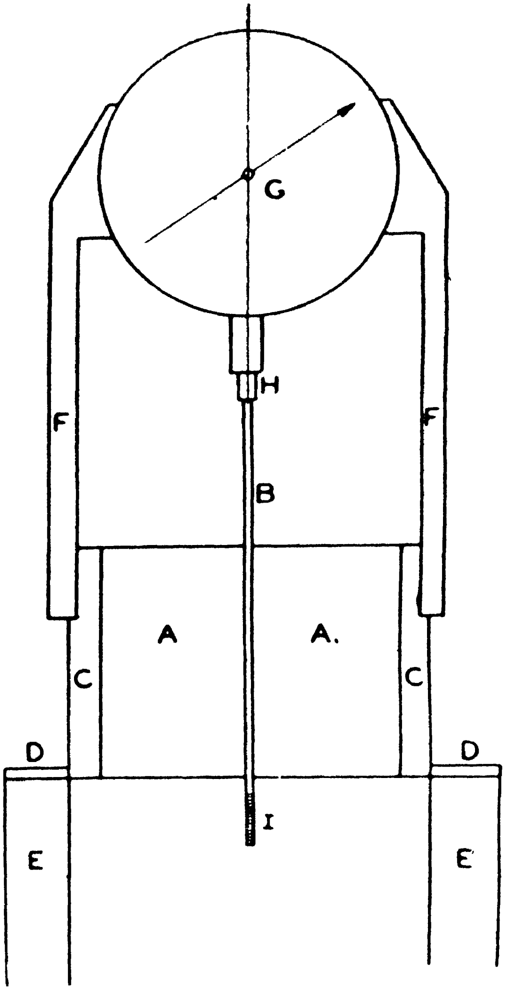

FIG. 1 (XII^3)
Pochettino's moving cylinder viscometer

Pochettino's[1] falling co-axial cylinder viscometer is suitable for accurate viscosity determination of substances of the nature of pitch. It requires large amounts of testing material and the actual test is slow since a long interval is required in the cooling: Traxler and Schweyer[2] worked out the best conditions for rapid estimation with small amounts of material. An instrument conforming to the criterion of the above authors has been developed by Pugh.[3] It provides a simple, quick, and accurate method for the measurements of viscosities of materials within the range 5 × 10^4 to 10^{11} poises.

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[1] *Loc. cit.*

[2] Amer. Soc. for Testing Materials, *Proc. of 39th Annual Meeting*, 1936, *36*, 523.

[3] *J. Scient. Inst.*, 1944, 21, 177.

Rotating Cylinder Apparatus. This type of instrument consists of two concentric cylinders, the annulus between them being filled with the fluid the viscosity of which is being measured. One of these cylinders (for instance, the outer one) is then rotated at a constant angular velocity, and the torque needed to maintain this constant rotation is determined. If the given fluid be viscous then, at constant temperature, the following equation holds :

$$\eta = \frac{T}{4\pi\omega l}\left(\frac{1}{r_1{}^2} - \frac{1}{r_2{}^2}\right),$$

where η = coefficient of viscosity of the fluid ; T = torque needed to maintain the constant rotation ; ω = angular velocity ; l = length of immersed cylinder ; r_1 and r_2 = radii of inner and outer cylinders respectively. This equation applies strictly to portions of an infinitely long cylinder-system. In actual instruments ' end-effect ' must be eliminated by special design, or an allowance must be made for it in the process of calculation.

If the torque, T, is measured by suspending the inner cylinder by means of a wire of restoring moment N, and the angle, θ, through which this wire is deflected, is determined, then :

$$T = N\theta,$$

so that

$$\eta = \frac{N\theta}{4\pi\omega l}\left(\frac{1}{r_1{}^2} - \frac{1}{r_2{}^2}\right)$$

which also shows that for a given fluid, of viscosity η (temperature being constant), there is a straight-line relationship between the deflection, θ, and the angular velocity, ω. If, therefore, for a given apparatus, deflections θ and θ_1 are obtained for two different liquids at the angular velocities of ω and ω_1 respectively, the relationship between their viscosities, η and η_1, is

$$\frac{\eta}{\eta_1} = \frac{\theta\omega_1}{\theta_1\omega}$$

The linear relationship between θ and ω, for a given liquid, in a given apparatus, holds until a certain limiting value of ω is reached.[1] At this point turbulent motion sets in, and the relationship then ceases to be linear.

The Hatschek modification of the Couette apparatus (which is of the concentric cylinder type) was used by Sibree[2] in accurate work on the viscosities of emulsions. The modified apparatus is illustrated in Fig. 2 (XII^3) ; here A is the inner cylinder (which, in one model, is 10 cm. in diameter) which is suspended by means of a wire B. E′ is a ' guard cylinder ' for the purpose of preventing the drag exerted by the bottom of the outer cylinder (diameter 11 cm.) from being communicated to the inner one. E is a similar guard cylinder for eliminating the effects of the liquid surface. The guard cylinders have edges chamfered at an angle of under 45°, there being a clearance of 2 mm. between these chamfered edges and corresponding parallel edges on the cylinder A. Further protection from ' bottom-effect ' is provided by a thin, circular plate H, fixed as shown, the diameter of which is 2 mm. less than the internal diameter of the outer cylinder D.

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[1] See Richardson, *Kolloid-Z.*, 1933, *65*, 32.

[2] *Trans. Faraday Soc.*, 1930, *26*, 26 ; *ibid.*, 1931, *27*, 161.

The guard cylinders are supported by three vertical rods (only two of which can be shown in the side view) which are fixed in an eccentric ' centering-head ' at the top of the apparatus, and which pass through three circular slots (see plan) in the cylinder A. This allows deflections up to an angle of 100°. In practice, however, much smaller deflections are used.

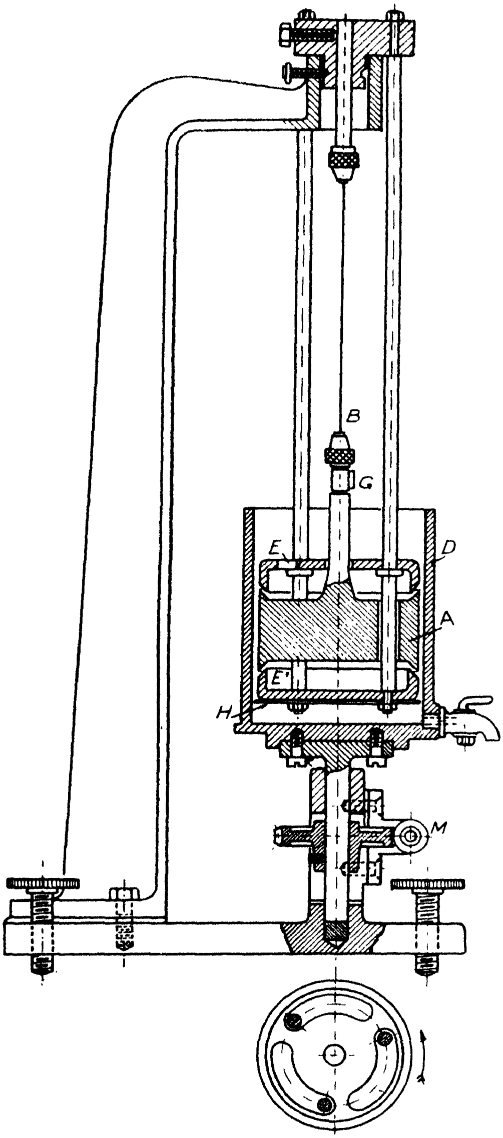

FIG. 2 (XII^3)
Hatschek's concentric cylinder apparatus

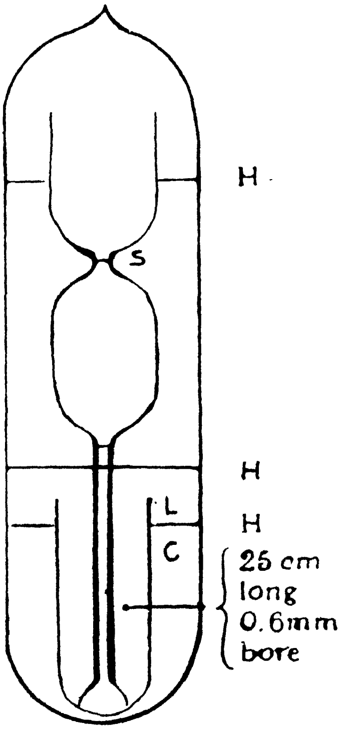

FIG. 3 (XII^3)
Closed viscometer of Plank and Hunt

The whole system of suspended cylinder and guard cylinders should be centred before commencing a determination. M is a worm-geared driving mechanism for rotating the outer cylinder. Deflections are read by the use of a telescope and scale in conjunction with a small mirror. Temperatures around room-temperature are readily maintained for sufficient intervals of time by lagging the outer cylinder with heat-insulating material. The complete apparatus may also be enclosed in an electrically heated wooden chamber, fitted with a thermo-regulator, and with a small electric fan to maintain circulation.

Using the apparatus just described, it is found that the linear relationship between deflection and angular velocity holds, for liquids of kinematic velocity equal to or greater than that of water, until an angular velocity of about 100 degrees of arc per second is reached. At angular velocities greater than this, turbulent motion sets in. For routine testing purposes, modified forms of viscometer have been developed, in which the constant torque has been replaced by the torsional control of a twisted wire. The American 'Doolittle' viscometer, which operates on this principle, was expressly designed for the testing of ordinary cream. The British 'Technico Universal' viscometer, which works on the same principle, has interchangeable parts by virtue of which it may be used for a wide variety of routine control determinations. These torsion viscometers operate simply and rapidly, but a high degree of accuracy is not guaranteed. They are of value in such testing where results accurate to ± 0·5 per cent are deemed satisfactory.

Viscosity Determination in a Closed System. For the determination of the viscosity of liquid ammonia an apparatus similar to that shown in Fig. 3 (XII^3) has been devised by Plank and Hunt.[1] The apparatus was calibrated with dry carbon disulphide and carbon tetrachloride as standards. The viscosities and densities of compounds used were:

Temp.	Carbon disulphide		Carbon tetrachloride	
	Density	Viscosity	Density	Viscosity
5°	1·2856	0·004125	1·6230	0·01233
15°	1·2750	0·003805	1·6037	0·010476
25°	1·2554	0·003565	1·5843	0·009027

The following is a description of Plank and Hunt's experiments.[2] The constants, C and C′, of the equation:

$$\eta = C\rho t - C'\rho/t$$

were determined at each temperature. The ammonia was dried over sodium and distilled under reduced pressure into the apparatus. After the outside jacket was sealed the apparatus could be rotated in order to fill the viscometer with the liquid. The supports, H's, held the viscometer perfectly vertical and rigid within the jacket when the outside jacket was placed in a vertical position. The determinations were made in an air thermostat whose temperature was regulated to 0·05°. The time was measured with an accurately calibrated stop-watch.

The apparatus was designed as shown because a closed system was necessary, and by having container C full of liquid when the meniscus passes S, a constant head was ensured. A fine lip, L, on C ensured a delivery of the liquids at the same level, so that a change in surface tension of the liquids did not interfere. The small head also increased the time of flow. It is difficult to fill the apparatus with cold ammonia by distillation and get the desired hydrostatic head when the liquid becomes warm. Two viscometers were used and the results are in excellent agreement. The viscosities and densities at the three temperatures are :

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[1] *J. Amer. Chem. Soc.*, 1939, *61*, 3590.

[2] *Loc. cit.*

Temp. ° C.	Density g./ml.	Viscosity	Viscosity of ammonia g./cm. sec.
5°	0·63197	0·001617	0·001618
15°	0·61821	0·001454	0·001457
25°	0·60427	0·001350	0·001350

The viscosity of liquid ammonia is reported by Stakelbeck[1] to be 0·00218 g./cm. sec. at 20°, 0·00229 at 10°, 0·00238 at 0°, and 0·00252 at − 20°.

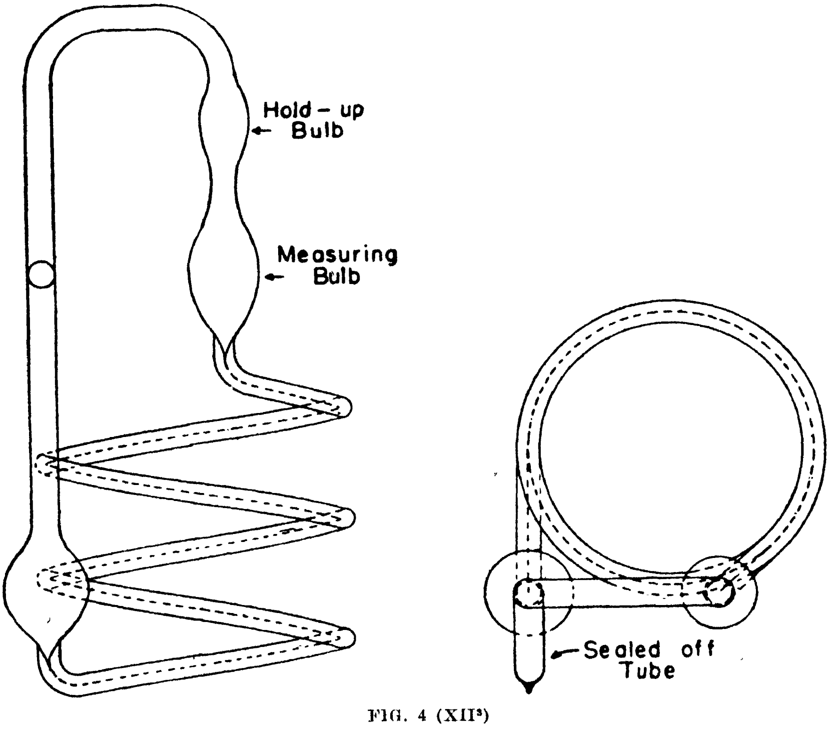

FIG. 4 (XII[3])
Sealed viscometer of Edwards and Bonilla

He used the Lawaczec falling-ball method. At − 33·5° two values are reported, 0·002543 poise[2] and 0·00260 poise.[3,4]

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[1] *Z. kalte-Ind.*, 1933, *40*, 33–40. [2] Fitzgerald, *J. Phys. Chem.*, 1912, *14*, 621.
[3] Elsey, *J. Amer. Chem. Soc.*, 1920, *42*, 2454. [4] Quoted by Plank and Hunt, *loc. cit.*

Viscosity of Butadiene. A special sealed viscometer (Fig. 4 (XII^3) has been employed by Edwards and Bonilla [1] for the determination of the viscosity of butadiene. On account of its low viscosity, the end-effect correction would be high in the ordinary Ostwald apparatus. On account of its long helical capillary pressures above atmospheric can also be used with their sealed apparatus. The capillary has a length of 63 cm. and a diameter of 0·057 cm. The coils were 7 cm. each. The measuring-bulb holds 2·80 ml. and had thick walls which would not expand appreciably under pressure. The total charge was approximately 4·1 ml. The average head during a run was between 7 and 8 cm. The hold-up bulb is desirable to obtain smooth operation at the start of the run. The opening between it and the measuring-bulb should not be very small, about $\frac{3}{16}$ in. is, according to the authors, satisfactory. Calibration was carried out with distilled water at room temperature and with pure diethyl ether which has a viscosity approaching that of butadiene from 20° to 75°.

Measurement of the Consistency and the Viscosity of Emulsions. For the determination of the consistency of an emulsion, the Mobilometer [2] may sometimes be used. In the form originally described (*see* Fig. 5 (XII^3)) it consists of a brass cylinder, 22·85 cm. long, and 3·89 cm. in internal diameter. The base is detachable, to facilitate cleaning. The assembly is fixed by screws to a baseboard which, during a determination, should be properly levelled (*Note.*—Some instrument-makers supply the apparatus fitted with a spirit level and with levelling-screws). In use, the viscous liquid is poured into the cylinder until it reaches a mark on the inside, 2 cm. from the top. When thus filled, a plunger is allowed to fall through the liquid, and the time of fall, in seconds, is noted. The plunger is 50·8 cm. long, 0·635 cm. in diameter, carries a small platform, for the addition of weights, at the top, and is fitted with a disk, 3·81 cm. in diameter and 0·08 cm. thick, at the bottom. In one arrangement, the plunger and its fittings are made completely of brass, and the disk carries 51 holes, each 0·153 cm. in diameter. In another arrangement, the brass plunger is fitted with a brass disk without holes. A third arrangement consists of a plunger and fittings made completely of aluminium, the disk carrying 51 holes. The weight of the moving parts, in the case of the brass plunger, platform, and perforated disk, is approximately 75 grams. In the case where aluminium is used, the moving parts weigh 33 grams. (*Note.*—As supplied by some instrument-makers the moving parts, with the platform carrying no load, weigh 100 grams. An additional disk, with 4 holes, each 6·25 mm. in diameter, is sometimes supplied.) Each disk is fitted at the base with a tip, 0·85 cm. long, to prevent contact between the disk itself and the bottom of the cylinder. The total fall, therefore, through the liquid is one of 20 cm. The supporting and guiding bracket is practically frictionless. Measurements may be made, for example at 20° C., by inserting the plunger-assembly to be used, and forcing it down into the liquid, until the tip makes contact with the bottom of the brass cylinder. It is then raised until the base of the disk lies in contact with the surface of the liquid, and allowed to fall freely, the time of this fall being taken by means of a stop-watch. The readily audible click, which occurs when the bottom of the cylinder is touched by the tip, assists in the timing. The procedure may be repeated with a loaded platform (viz. loads of 100, 300, 600 grams may be placed on top). The results may then be graphed, and the graphs obtained may be used for comparative purposes. In improved forms, the apparatus is provided with a special water-jacket, enabling tests to be carried out at different temperatures.

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[1] *Ind. Eng. Chem.*, 1944, *36*, 1039.

[2] Gardner and Van Heuckeroth, *Ind. Eng. Chem.*, 1927, *19*, 724.

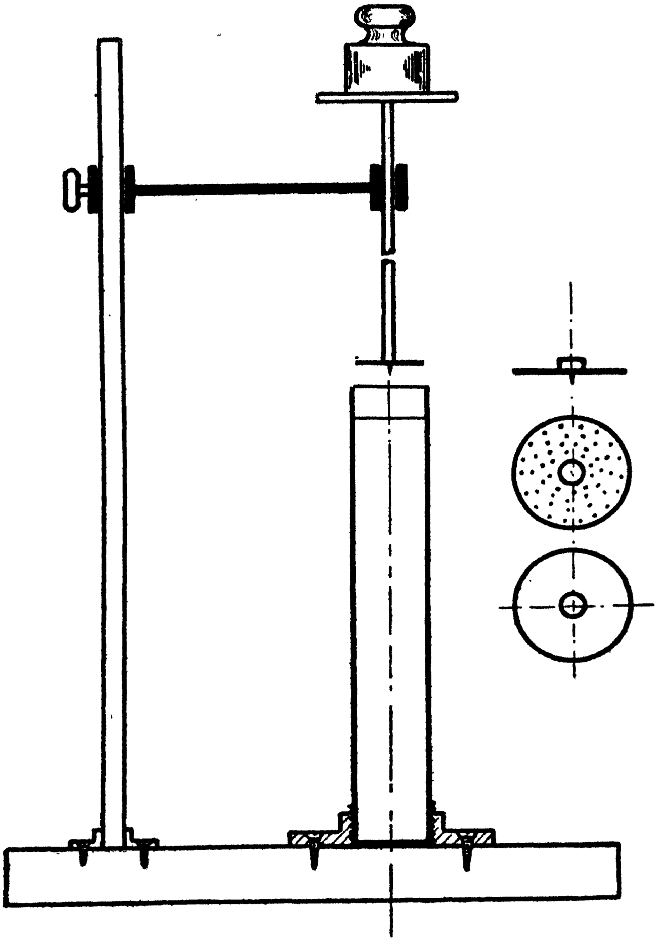

FIG. 5 (XII^3)
The mobilometer for measurement of the consistency of an emulsion

The Pentrameter.[1] This instrument, which was designed to compare the consistencies of thick emulsions, consists of a plummet, 16·5 cm. long and 1·5 cm. in diameter, made from solid synthetic amber. It tapers off, 0·8 cm. from the lower end, to a point. The upper end is fastened to a vertical metal rod, 21·2 cm. long and 0·6 cm. in diameter. A pointer is fitted near the top of the metal rod to indicate, on a scale held parallel to the rod, the depth to which the emulsion is being penetrated by the amber plummet. The metal rod is supported, when not in operation, by a spring clamp. On release of the clamp, the plummet drops vertically (the vertical fall being ensured by the use of a stationary guide) through the emulsion in a suitable container. Initial penetration of the emulsion having taken place, the time taken for penetration through a depth of 2 cm. (e.g. from the 8-cm. to the 10-cm. marks on the scale) is measured by means of an electrical stop-watch. The apparatus may also be used to indicate the effect of ageing on the consistency of a thick emulsion.

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[1] Hall and Dawson, *Ind. Eng. Chem.,* 1940, *32,* 415.

CHAPTER XIII [3]

ADSORPTION

SECTION 1: ADSORPTION TECHNIQUE

ADSORPTION is a phenomenon requiring a two-phase system to function. It implies that a change in concentration of the disperse system at the interface takes place. It consists in the attachment to the solid or liquid of a layer of one or more molecules in thickness. The phenomenon is essentially a surface effect and is a function of the specific surface (i.e. the surface area per unit volume). In the case of ' smooth ' area this can readily be interpreted but in the case of ' rough ' surfaces it is more difficult to give a quantitative measure. While the term adsorption is restricted to surface effects, solution in the interior of the substance is called absorption. McBain has suggested the adoption of the term *sorption* (a term now generally used) to include the whole phenomena of the taking up of a gas by a solid. Adsorption is particularly in evidence in the case of highly porous solids or finely divided substances. Adsorption is increased by high concentration in the disperse phase and by high pressure in the case of gases. When not accompanied by chemical changes adsorption is reversible and selective. (See Vol. II, Chap. V, pp. 199–203.)

Use of Small Glass Spheres in Adsorption from Non-aqueous Media. The results obtained with powdered solids are difficult to interpret because of the uncertainty of the surface area and of possible selective adsorption at sharp edges, corners, &c. With uniform spherical particles these difficulties would not arise. Urbanic and Dammerell [1] describe a method of preparing such spheres of glass and used them to study the adsorption of iodine from carbon tetrachloride solution. Soda-lime glass tubing was powdered in an iron mortar and digested with hot 6 N hydrochloric acid eight times. The powder was washed with water and alcohol and allowed to dry in the air ; it was then vacuum dried at room temperature for 3 hours. A stream of the powdered glass was then passed through a large blow-pipe flame. The oxygen supply was by-passed to the flame through an apparatus consisting of a capillary 1·5 cm. by 1 mm. inside diameter, next a tube 10 cm. long and 5 mm. internal diameter and containing the powdered glass, then through a capillary like the former one into a wider tube 7·5 cm. long and 1·25 cm. diameter where large particles of glass settled down and from which 5-mm. tubing led to the blow-pipe. Two taps on a **T**-piece allowed the oxygen to be sent directly or through the by-pass at will. The pieces of molten glass were allowed to fall through 17·5 cm. of air before dropping into pure cold carbon tetrachloride contained in a

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[1] *J. Phys. Chem.*, 1941, *45*, 1245.

20-cm. diameter evaporating-dish filled to the brim, so that all the particles collected fall straight into the liquid ; it was hoped in this way to avoid the adsorption of air or water on the spheres. About 0·4 gram of spheres was projected into 200 ml. of carbon tetrachloride at a time. (50 grams of powder gave 30 grams of spheres yielding 7 grams of uniform material after fractional sedimentation.)

A sample of each batch was examined microscopically and was discarded if the departures from sphericity exceeded 15 per cent. The satisfactory batches were bulked and passed through the flame a second time, which increased the percentage of spherical particles. The particles were then fractionated by sedimentation twenty times in a 50-ml. alkali burette, rejecting the largest and smallest spheres. The diameters of the spheres were measured microscopically. A small suspension was placed on a slide and the liquid allowed to evaporate. The diameters of 500 particles were determined with a calibrated ocular micrometer with the slide on a mechanically movable stage : 92 per cent were spheres and the diameters were found to lie between 40 and 80 microns. The surface area and volumes were calculated from the diameters. The density of about 6 grams of spheres was determined in a 5-ml. pyknometer. From the weight of spheres used in an experiment and the determined density of 2·45 the volume of the spheres could be found and then using the results of the microscopic examination that a volume of $5{\cdot}477 \times 10^{-5}$ ml. of spheres corresponds to a surface area $540{\cdot}9 \times 10^{-4}$ sq. cm. the surface area of the weight of spheres used experimentally can be determined.

The spheres were tested by the adsorption of iodine from carbon tetrachloride with the following results :

6·901 grams of glass spheres used having a surface area of 2,780 sq. cm.

Concentration of iodine solution	Number of grams of iodine adsorbed
$2{\cdot}12 \times 10^{-5}$ M	$8{\cdot}9 \times 10^{-5}$
$7{\cdot}28 \times 10^{-5}$ M	$8{\cdot}8 \times 10^{-5}$
$2{\cdot}00 \times 10^{-4}$ M	$9{\cdot}2 \times 10^{-5}$

If the layer is monomolecular and the radius is $1{\cdot}97 \times 10^{-8}$ cm., it is calculated that 39·2 per cent of the surface is covered.

The glass spheres were always in the carbon tetrachloride until the experiment was completed and the iodine left in the liquid was determined colorimetrically.

Adsorption of Hydrocarbons with Silica Gel. A series of experiments conducted by Mair and White [1] showed that (*a*) aromatic and olefin hydrocarbons could be completely removed from paraffin and naphthene hydrocarbons, but the capacity of the gel as an adsorbent of the one olefin (diamylene) investigated was only one-third of its capacity as an adsorbent of the aromatic hydrocarbons ; (*b*) the capacity of silica gel as an adsorbent of the aromatic hydrocarbons was found to depend on the concentration of the solution, and also, to some extent, on the components of the solution from which the aromatic hydrocarbon is being adsorbed. The amount of *o*-xylene, for example, adsorbed from a 10 per cent solution of that aromatic in *n*-nonane being about 12 to 13 ml. per 100 grams of gel and approximately the same for gel of different grain size ; (*c*) a small but definite separation of naphthene from paraffin hydrocarbons, the naphthenes tending to be adsorbed by the gel in preference to the paraffins ; (*d*) a slight separation of normal paraffin hydrocarbons of different molecular weights, the paraffin of low molecular weight being adsorbed in preference to that of high molecular weight ; (*e*) under the conditions of these experiments, silica gel did not crack or otherwise attack aromatic, naphthene, or paraffin hydrocarbons.

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[1] *J. Res. Nat. Bur. Standards*, 1935, *15*, 51.

Apparatus and Materials. The apparatus is simple, consisting of glass tubes mounted vertically and filled with silica gel. One of these tubes is shown in Fig. 1 (XIII^3). At the top is sealed a glass bulb as a reservoir for the hydrocarbon mixture. To the top of this reservoir may be attached a rubber tube through which air pressure may be applied during filtration. At the bottom of the adsorption tube is sealed a smaller tube which extends into a stoppered graduated cylinder. A small plug of glass cotton at the bottom of the adsorption tube suffices to hold the silica gel in place. The adsorption tubes used in the experiments were 40 cm. long and had an inside diameter of 1·5 to 1·7 cm. Two grades of silica gel were used, (40–200 mesh) coarse and (200 mesh and finer) fine. The gel, after use and after displacement of the oil with water, was reactivated by transferring it while wet to a Pyrex glass tube, sucking it as dry as possible and placing it in an oven where it is heated for 24 hours at a temperature of 300° to 350° while air is aspirated through it.

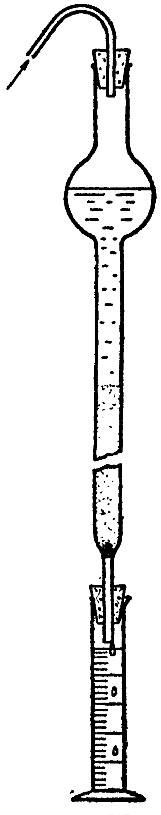

FIG. 1 (XIII^3) Adsorption tube

The separation of different types of hydrocarbons of high molecular weight has also been made by Willingham by adsorption on silica gel. In his original paper [1] references to earlier work on this subject are recorded. The apparatus described in this paper by him is in the main similar to that recorded by Mair and White.[2]

The procedure adopted for the experiments is as follows : To a weighed amount (20 to 25 grams) of one component in a small flask is added a weighed amount of the second component to produce a mixture of the desired concentration. The components are then melted by placing the flask on a steam-bath and thoroughly agitated to ensure homogeneity. After the refractive index has been determined, the mixture is transferred to the filtering-tube, and allowed to filter, under an air pressure of about 4 lb./in.^{2} through 50 cm. (approximately 20 grams of loosely packed gel.) In most experiments the filtering-tube and receiver were kept at approximately 100° by passing steam through the jacket. A small gas flame from a bunsen burner was used as needed, to keep the material in the upper bulb liquid. The filtrate was collected in a number of small fractions, and the refractive index of each determined. To displace the adsorbed material from the gel with water, toluene was passed through the column to displace the adsorbed hydrocarbons of high molecular weight, which were thus obtained in solution with the excess toluene. The bulk of the toluene was subsequently separated from the wanted hydrocarbons by simple distillation, with the last traces of toluene being removed at 120° to 130° by sweeping with a small stream of carbon dioxide.

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[1] *Ibid.*, 1939, *22*, 321.

[2] *Ibid.*, 1935, *15*, 51.

A sharp separation of 5-(7-tetrahydronaphthyl)-docosane from 5-(2-decahydronaphthyl)-docosane, and *n*-dotriacontane from 1-(*p*-diphenyl)-octadecane was obtained. Some separation of 1-(*p*-diphenyl)-octadecane from 5-(7-tetrahydronaphthyl-docosane) was found, but the separation was not as sharp as with the two preceding mixtures. No separation of a mixture of *n*-dotriacontane and 5-(2-decahydronaphthyl)-docosane was found.

The capacity of 20 grams of silica gel to adsorb preferentially the more aromatic components of these mixtures was found to be 1·8, 3·3, and 0·8 gram, respectively, for the first three mixtures listed above.

Gibbs' Equation

If σ = free surface energy per unit area of interface, where one of the phases (e.g. a liquid) contains a single dissolved substance
a = area of interface
μ = chemical potential of the dissolved substance
s = difference between the concentrations of the dissolved substance at the interface and in the body of the solution
z = thermodynamic potential of the system,

then, by thermodynamical reasoning,

$dz = \mu . ds + \sigma . da$, where dz represents an increase. Since dz is a perfect differential, it follows that

$$\left(\frac{d\sigma}{ds}\right)_a = \left(\frac{d\mu}{da}\right)_s \quad . \quad . \quad . \quad . \quad . \quad . \tag{1}$$

Also since μ, a, and s are variables, we have

$$\left(\frac{d\mu}{da}\right)_s \times \left(\frac{ds}{d\mu}\right)_a = -\left(\frac{ds}{da}\right)_\mu \quad . \quad . \quad . \quad . \tag{2}$$

From equations (1) and (2), it may be shown that

$$\left(\frac{d\sigma}{d\mu}\right)_a = -\left(\frac{ds}{da}\right)_\mu \quad . \quad . \quad . \quad . \quad . \tag{3}$$

Equation (3) was deduced by Willard Gibbs in 1874. Also, it may be shown that, for dilute solutions,

$$d\bar{\mu} = \mathrm{RT}\frac{dc}{c} \quad . \quad . \quad . \quad . \quad . \quad . \tag{4}$$

where $\bar{\mu}$ = molecular chemical potential ; R = 'gas' constant ; T = absolute temperature ; c = concentration. By a combination of equations (3) and (4), if s be expressed in gram-molecules, we find that

$$\mathrm{U} = -\frac{c}{\mathrm{RT}}\left(\frac{d\sigma}{dc}\right)_a \quad . \quad . \quad . \quad . \quad . \tag{5}$$

where U = ' adsorption excess ', in moles, per unit surface, i.e. the mass of substance, per unit interface, in excess of the mass which would be there if capillary effects were absent.

From equation (5), if $\frac{d\sigma}{dc}$ be positive, $-$ U will be negative, and conversely. This indicates that if a substance would, on adsorption, lower the interfacial tension, it will tend to be adsorbed.

Adsorption at Liquid Interfaces. The first general guide to the study of adsorption at liquid interfaces was provided by Gibbs, who from purely thermodynamic considerations worked out the well-known adsorption isotherm. See equation (5) above.

Earlier methods for testing this equation for the gas-liquid interface depended on passing a stream of bubbles through the solution under investigation. From the number and size of the bubbles passing and the measured increase of solute concentration in the liquid obtained by collapsing them, the adsorption could be calculated. Donnan and Barker,[1] the earliest workers in this field, used a vertical column in which the stirring effect of the stream of bubbles was believed to be prevented by a system of baffle plates, and obtained good agreement with theory for the adsorption of nonylic acid from aqueous solution. Their technique has, however, been severely criticized by McBain and Dubois,[2] who passed the bubbles through an inclined tube and analysed the liquid from the collapsed films interferometrically.

Nitrogen from a cylinder fitted with a constant-pressure regulator is purified by passing through aqueous sodium hydroxide and is then saturated with the vapours of the solution which is to be measured, first by bubbling it through a sample of that solution and then by passing it through a Washburn saturator filled with another sample of the same solution for final adjustment. The pressure is steadied by a capillary-tube, after which the gas bubbles into the apparatus through a suitably designed jet. The bubbles slowly pass up the long, inclined tube and rapidly up the narrower vertical tube, each pushing the previous ones out of the top of the liquid towards the vessel where the liquid from the collapsed films collects. From here the nitrogen, still saturated with the vapours from the solution, passes through a Parkinson and Gowan flow-meter, previously calibrated by passing through it a known volume of air from a large gas holder. It was found that the volumes recorded by this instrument differed from the true values by less than 1 per cent.

The apparatus of McBain and Dubois [3] is shown diagrammatically in Fig. 2 (XIII[3]). It consists of a system S_1, S_2, S_3, for saturating the nitrogen, an ' adsorption-tube ' CD ending in the short vertical draining-tube EF and a receiver B_2.

Nitrogen from a cylinder equipped with a pressure regulator is freed from carbon dioxide present by passage through strong potassium hydroxide solution in the gas-washing bottles A, A. From these it passes in a steady stream of bubbles through the saturators where it comes into equilibrium with a solution of the same concentration as that in the adsorption-tube. The mercury manometer M is connected as shown. The capillary-tube serves to regulate and steady the flow of gas through the rest of the apparatus.

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[1] *Proc. Roy. Soc.*, 1911, *85A*, 557.

[2] *J. Amer. Chem. Soc.*, 1929, *51*, 3534; see also McBain and Davies, *ibid.*, 1927, *49*, 2230.

[3] *Loc. cit.*

A constant stream of bubbles of the same size is formed at the specially shaped bubbling-nozzle N and passes slowly along the tube CD filled with a solution of the solute whose adsorption is to be determined. Here adsorption, if any, takes place at the surface of the bubbles. Each bubble finally rises through the tube EF, where it joins a column of nearly cylindrical, rapidly draining films, which are continually passing over the bend at F and being replaced from behind. The time required for passage along the tube CD is about 12 seconds, for the tube EF about 1½ seconds.

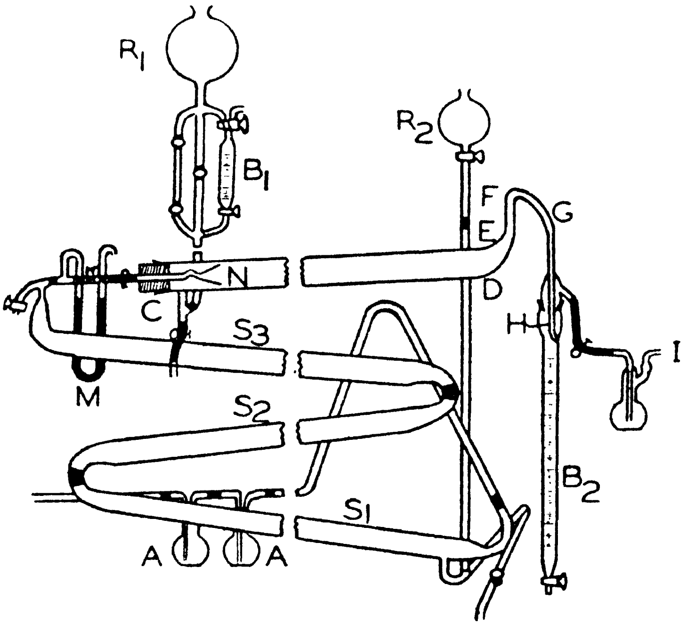

FIG. 2 (XIII³)
Saturation apparatus

The films with their adsorbed surface layers collapse in the descending-tube FGH, and the liquid from these collects in the receiver B_2, which is a 100-ml. burette attached to GH by a ground-glass connexion and equipped with a large-bore glass stop-cock for rapid emptying. The nitrogen released by collapse of the bubbles leaves the apparatus at I and passes through a gas meter (Boys bell meter). The end of the tube GH was bevelled and bent so as to touch the side of the burette. The effect of this detail was to cause the complete collapse of any films which had reached this orifice still unbroken. The end of the burette outlet was cut off close to the stop-cock to reduce the amount of liquid remaining in this part.

The reservoirs, R_1 and R_2, are for supplying liquid to the adsorption and the saturating tubes, respectively. The means of emptying the apparatus are shown in the drawing.

DIMENSIONS OF THE APPARATUS

	Tube		
	CD	EF	S_1, S_2, S_3
Inside diameter, cm. . .	2·5	0·86	1·8
Length, cm.	156	8	120
Slope, per cent . . .	4–8	vertical	8

In general, results obtained by this method are almost without exception much higher than the values calculated from the Gibbs equation. The causes of the discrepancy are not known, though McBain states that wide variations in adsorption are caused by variations in the size and speed of the bubbles.

This source of error is completely eliminated in the static method devised by McBain and Humphreys.[1] The solution under examination is contained in a long silver trough, shielded from evaporation, and the surface layer ($\frac{1}{10}$ mm.) is removed by drawing a micrometer blade at high speed over it. The film of liquid removed is collected in a cylinder mounted on the carriage carrying the blade, and analysed.

For a full description of the very elaborate equipment necessary to carry out in practice this basically simple idea the reader is referred to the original papers. Unlike all the dynamic methods, it gave results in good agreement with the calculated values for the positive adsorption of phenol and hydrocinnamic acid and the negative adsorption of sodium chloride. McBain concludes that the Gibbs equation is a limiting law obeyed by static surfaces.

For the study of adsorption at liquid-liquid interfaces an apparatus of the moving-bubble type may be used, with modifications suited to the liquids under examination. Gibby and co-workers [2] describe types suited to the study of the adsorption of dyes at water-hydrocarbon and water-mercury interfaces. The interfacial tension was determined by means of the drop pipette, the values of σ and $\frac{d\sigma}{dc}$ being calculated from smoothed curves of drop number plotted against concentration. Here also the experimental results were at variance with the predictions of the Gibbs equation, presumably owing to the existence of such factors as electrical double layers of which the Gibbs equation takes no account.

The Adsorption Isotherm.

Extension of a Surface. Suppose we have a film of surface area

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[1] *J. Phys. Chem.*, 1932, *36*, 300; *Proc. Roy. Soc. A.*, 1936, *154*, 608.
[2] *J. Chem. Soc.*, 1936, 119; *ibid.*, 1940, 596.

a which, at a temperature T, has a surface tension of value σ. Then we may perform the following reversible cycle:

(α) Keeping T steady, increase *a* by *da*. The work, δA_E, done in this process $= -\sigma . da$.

(β) Cool to $T - dT$, keeping the area constant. As a result of this operation the surface tension reduces to a value $\left\{\sigma - \left(\frac{d\sigma}{dT}\right).dT\right\}$.

(γ) Allow the film to contract until its area has the original value *a*. The work, δA_C, done in this process $= \left\{\sigma - \left(\frac{d\sigma}{dT}\right).dT\right\}da$.

(δ) Increase the temperature to the original value T.

On the whole, the work, δA, done by the system $= \delta A_C + \delta A_E$.

$$= \left\{\sigma - \left(\frac{d\sigma}{dT}\right).dT\right\}da - \sigma . da,$$

$$= -\left(\frac{d\sigma}{dT}\right)dT . da = \text{heat absorbed, } dQ.$$

If the latent heat of extension of a surface (i.e. the heat absorbed when the surface is extended isothermally by 1 square unit) $= l_E$, then, as Lord Kelvin showed,

$$l_E = -T\left(\frac{d\sigma}{dT}\right).$$

Pure water, at 15° C., has a surface tension of 73 dynes/cm. (approximately). In the case of water, the coefficient of increase of surface tension with respect to temperature $\risingdotseq -0{\cdot}015$. Hence,

$l_E = (-288) \times (-0{\cdot}015)$, approximately.

$\risingdotseq 43$ units, which is numerically about half the value of σ.

In such a case, therefore, the heat absorbed would be roughly equal to half the work done in the process of extension.

The heat absorbed when 1 gram of a liquid, of density ϱ, is changed from the condition of a plane surface to that of a drop of radius $r = \frac{2T}{r\varrho} . \frac{d\sigma}{dT}$.

Excess Pressure inside Droplet. The excess pressure inside a droplet is given by the expression $\frac{2\sigma}{r}$, where σ and r have the same meaning as above. In order that this excess pressure should vanish, either σ should become zero, or (and) r should become large. When σ represents an interfacial tension between a dispersed liquid phase and the continuous liquid phase, the greatest stability, in the thermodynamic sense, will obtain when $\sigma = 0$. This condition, however, is usually associated with complete miscibility of the two liquids. On the other hand, r might be made to increase by the coalescence of a number of droplets. Even this phenomenon alone would have the effect of diminishing the free energy of such a system, and would tend to promote a greater degree of stability, in the thermodynamic sense.

Langmuir and Waugh[1] explained how stable O/W emulsions are possible when σ, the interfacial tension, becomes zero.

Antonoff's Rule. According to this rule, the interfacial tension between two liquids, in equilibrium, is equal to the difference between their individual liquid/vapour surface tensions. The rule has been confirmed in some cases, but deviations are known. The rule does not hold for non-spreading liquids, nor does it hold for those liquids which possess a high initial spreading coefficient (*see* under Adhesional Work and Spreading) with respect to the second liquid. Deviations from Antonoff's rule are measured by the value of the expression:

$$\frac{\text{Actual interfacial tension} - \text{Calculated interfacial tension}}{\text{Actual interfacial tension}}$$

Deviations are found to be greater at lower temperatures, but they are not found to be related in a simple manner to molecular structure.

Adhesional Work and Spreading. The spreading, on a liquid surface, of another liquid, is the result of two opposing tendencies—adhesion and cohesion. Dupré, in 1869, showed that the "adhesional work", W_A, involved in the approach and contact of two surfaces, is given by the equation:

$$\begin{aligned} W_A &= \sigma_1 + \sigma_2 - \sigma_{1,2} \\ &= -\Delta\gamma \end{aligned}$$

where σ_1 and σ_2 are the free energies of the two surfaces, which free energies are measured by the surface tensions, and $\sigma_{1,2}$ is the free energy at the interface which, in turn, is measured by the interfacial tension. $-\Delta\gamma$ is the diminution in free energy when contact is effected.

(*Note.*—A surface- or an interfacial-tension is, dimensionally, given by the expression:

$$\frac{M}{T^2}$$

'Energy per unit area' would have similar dimensions.)

If the two liquids are identical, the work of surface cohesion, W_C, $= 2\sigma$, or

$$\frac{W_C}{2} = \sigma$$

Harkins and others found, after a study of a number of liquid/water systems, that in most of the cases studied

$$\frac{W_A}{2} > \frac{W_C}{2}$$

The value of $(W_A - W_C)$, which was termed the 'spreading coefficient', was found to be an indication of the symmetry with which molecules lie in surfaces and interfaces. As examples, the spreading coefficient of acetic acid was found to be 45·20, of oleic acid 24·62, of hexane 3·41. If a polar group was present in any part of the molecule of an organic liquid, no matter how large the non-polar residue was, the polar group was found to increase very greatly the attraction between the organic liquid and water.

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[1] *J. Gen. Physiol.*, 1938, *21*, 745.

As examples of non-spreading liquids, the following may be quoted: the spreading coefficient of bromobenzene was found to be − 3·29, and of acetylene tetrabromide − 15·64. Harkins gave equations 'more closely related to molecular attractions than Dupré's', viz.

$$E_A = (\sigma_1 + l_1) + (\sigma_2 + l_2) - (\sigma_{1,2} + l_{1,2}) \quad . \quad . \quad (6)$$

$$= -\Delta E_S,$$

(where l_1, l_2, $l_{1,2}$ = latent heats of the surfaces and of the interface respectively

E_A = total energy of adhesion

E_S = total surface energy

and $$E_A = E_1 + E_2 - E_{1,2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Harkins and Ginsberg later showed that the spreading coefficient of a given liquid with respect to another liquid had two independent values, one value for initial spreading, and another (the final coefficient)[1] for the spreading over the contaminated surface when the liquids are mutually saturated. Thus the final spreading coefficient of carbon disulphide (on water), when the liquids were mutually saturated, was found to be − 9·95. According to Antonoff's rule, the value should be zero. Harkins held that the final spreading coefficient should always have a negative value.[2]

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[1] *See*, for example, Harkins, *J. Chem. Phys.*, 1941, *9*, 552.

[2] *See* article by Harkins and Cheng, *J. Amer. Chem. Soc.*, 1921, *43*, 35. Also *see* 'Note on Antonoff's Rule', by Yoffe and Heymann, *J. Phys. Chem.*, 1943, *47*, 409.

SECTION 2: ADSORPTION OF GASES

A typical apparatus for determining the adsorption isotherm of a gas on solids is described in Vol. II, p. 36. Like all of its kind, however, it suffers from the disadvantage that the 'dead space' in the bulb containing the adsorbent is difficult to determine accurately. Various methods have been tried, such as introducing helium or other inert gas whose sorption is likely to be negligible, but all such methods are subject to an element of uncertainty which can be particularly serious at high pressures and where only a small amount of gas is adsorbed. Moreover, since the experiment must be concluded whenever a reading is desired, it is not possible to observe the behaviour of the same specimen of adsorbent under different conditions of sorption, a fact which may in some cases lead to trouble.

The McBain-Baker sorption balance [1] offers an entirely new method of approach to the problem. It consists essentially of a fine silica spiral carrying a gold or platinum bucket for holding the adsorbent, and suspended in the bulb in which the adsorption experiments are carried out (Fig. 3 (XIII^3)). The spiral is calibrated directly at different temperatures before sealing into the bulb, which is then evacuated at a high temperature (450°) for 4–5 hours. Further manipulation depends on the isotherm being studied. Sorption of vapours at different partial pressures is studied by breaking a small bulb containing the liquid after preliminary evacuation of the tube. The upper part of the tube is enclosed in an electric thermostat at the desired temperature, and by altering the temperature of another thermostat enclosing the liquid in the bottom of the tube the pressure of the vapour can be adjusted to any desired value. Sorption of permanent gases can also readily be studied, and the balance is particularly valuable at high pressures, though here a buoyancy correction must be applied.

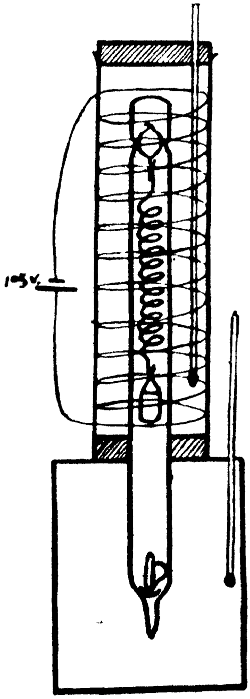

FIG. 3 (XIII^3)
McBain-Baker sorption balance

Since the extension of a helical spring is proportional to the cube of the diameter, coils of large diameter (2 cm. against the usual 1·25–1·5 cm.) may be used for very accurate work. In general, an extension of 4 cm. per gram is regarded as the minimum permissible sensitivity, which with a travelling-microscope reading to 0·001 cm. means that an increase of 0·00025 gram in the weight of the bucket can be detected.

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[1] *J. Amer. Chem. Soc.*, 1926, *48*, 690.

For all work with the sorption balance, and indeed with any type of adsorption apparatus, it is very advisable that after the preliminary evacuation the adsorbent should be charged with the gas or vapour under examination and again rigorously evacuated. The increased cleaning of the surface thus effected may make a considerable difference in the shape of the final isotherm.

Sorption as a Means of Determining Surface Areas. The Langmuir equation for the formation of a monomolecular adsorbed layer is

$$X = \frac{abp}{1 + ap}$$

where X is the adsorption in millilitres per 100 grams, p the pressure, and a and b are constants. In practice, this simple law, according to which completion of adsorption corresponds to an unbroken monomolecular layer on the surface of the adsorbent, is complicated by the occurrence of capillary condensation, so-called activated adsorption, and other effects. Nevertheless, the simplicity of Langmuir's deductions has led many workers to use his equation in attempts to determine the total available surface of powders and finely divided metals.

As far as adsorption from solution goes, all such attempts have so far proved to be fruitless. Thus the early results of Paneth and Radu [1] in which a reliable estimate of surface area was thought to be obtained from the adsorption of dyes in aqueous solution have been shown to be untenable by other workers, who found that sorption varied widely with changes in *p*H and nature of the dye used.

On the other hand, Emmett and his co-workers [2] have obtained a good deal of success in estimating the surfaces of metal catalysts by volume of various gases adsorbed at low temperatures. Owing to the heterogeneous nature of many catalysts it is essential to use gases which are completely inert towards the adsorbent and thus rule out the possibility of reaction. The chief difficulty, however, lies in determining the point at which formation of a monomolecular layer is complete. From various lines of evidence, both theoretical and empirical, Emmett concluded that the point at which the S-shaped isotherm flattened out corresponded to the complete formation of a layer one molecule thick on the surface of the catalyst.

Apparatus of standard design is used in making the adsorption measurements. In essentials it differs little from the usual type in which adsorption is measured from the change in volume of the gas admitted. The dead space surrounding the adsorbent is determined with pure helium, a procedure justified by the fact that at temperatures above 77° K. the adsorption of helium is always very small compared with that of the adsorbates being used. When the dead space has been determined the apparatus is again evacuated before admitting the gas under examination.

The area occupied by the adsorbed molecule is calculated from the density of the gas in the liquefied and solidified states. Values for the surface area obtained from the density of the liquefied gas are always slightly higher than those calculated from the density of the solid, but the agreement obtained with a wide range of permanent gases is good. By using high vacuum technique the application of the method, which as described above is only suitable for adsorbents having a surface of at least 400 cm.^{2}/gram, can be extended to substances having a smaller ratio of surface to mass. Armbruster and Austin[1] succeeded by this means in obtaining accurate values for the sorption of ethyl iodide on iron strips having an apparent surface of only about 30 ml. per gram. In view of the very small amount adsorbed, corrections had to be made for adsorption by the glass bulb in which the strips were contained.

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[1] *Ber.*, 1924, *57*, 1221.

[2] See *J. Amer. Chem. Soc.*, 1935, *57*, 1754, and following years.

Activated Carbon. The preparation of activated carbons suited to the enormous number and variety of processes to which they are applied in technical work is a distinct subject in itself. All methods have the twin object of increasing and cleaning the surface of the carbon, which may have been previously prepared (steam activation) or be liberated during activation (zinc chloride treatment). It will be considered briefly in the next section.

(1) *Activation with Free or Bound Oxygen.* The surface of carbon liberated by high-temperature distillation of carbonaceous materials of fine structure (wood, peat, some types of coal) is in the ordinary way covered with tarry products of distillation and hence rendered inactive. By treatment with air at 350°–500° and with steam at 800°–1,000° these adsorbed films are burned off, and further oxidation has the effect of increasing the available surface. It is essential that the temperature of formation of the primary charcoal should not be above 600°; the adsorbed hydrocarbon complex from higher distillation temperatures seems to be too firmly held to be removable by oxidation.

(2) *Activation with Zinc Chloride or Phosphoric Acid.* These methods are chiefly used on materials rich in cellulose or lignin, and appear to be based on a mechanism of dehydration. An ignition temperature of 300°–500° C. is used for zinc-chloride treated materials. Treatment with acid after activation removes the residue of zinc oxide, leaving the original structure largely undamaged, but cleaned of the bituminous products of distillation, which have been dissolved by the zinc chloride.

Treatment with phosphoric acid is extensively used with peat. The distillation temperature is high (1,000° C.) and a good deal of oxidation of the carbonaceous matter occurs, phosphorus distilling off.

(3) *Activation with Potassium Compounds.* Berl[2] gives interesting data on the comparative activities of the carbons made by heating different organic compounds of sodium and potassium to about 950° C. Potassium compounds were in all cases found to give better yields of more highly active carbons than the corresponding sodium compounds. The method is not, however, used on a technical scale.

The nature of the raw material, any pre-treatment it may have received, the method of activation and the temperature of treatment are only the chief of the many factors affecting the characteristics of the final product.

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[1] *Ibid.*, 1939, *61*, 1117.

[2] *Trans. Faraday Soc.*, 1938, 1040.

In general, for steam-activated carbons, the increase in activity is roughly parallel to the loss of material and is accompanied by a sharp fall in the bulk density. In charcoals intended for adsorption of gases the ideal aimed at is the production of very fine capillaries, giving great adsorptive power for gases and vapours. Such capillaries will probably be too small to allow the entrance of the large semi-colloidal particles commonly encountered in the decolorization of solutions, and in fact good gas-adsorbent charcoals (' A-chars ') are rarely suited for use as decolorizing carbons (' E-chars '), and conversely. X-ray studies show that the carbon in activated charcoals is not completely amorphous, but crystallizes in a modified graphite system. Activity depends on the surface structure of the particles, and on the unsaturated atoms or the lamina surface and edges.

The outstanding difference between activated charcoal and such adsorbents as silica gel lies in the hydrophobic nature of the former. Thus, whereas silica gel will preferentially take up water-vapour from air containing both water-vapour and ethylene, charcoal adsorbs the ethylene only. Decolorizing carbons act best in a hydrophilic medium, adsorbing hydrophobic substances or the hydrophobic parts of large molecules. This selective action is of great importance technically, and has led to the use of activated charcoals for such purposes as removing the traces of benzol present in washed coal-gas, or of phenols from effluent gas-works liquor. For such purposes the comparatively slight effect of temperature on adsorption (contrast the very great dependence on temperature of washing-out methods) and the high efficiency, even at very low partial pressures of vapour, are of particular value.

When a gas containing mixed vapours—for example, the benzol from gas retorts—is passed through a bed of charcoal, adsorption of all vapours present is initially, at all reasonable rates of flow, complete and instantaneous. As the charcoal becomes saturated the available surface decreases and finally, at the ' break-point ', traces of vapour can be detected in the issuing gas. If further quantities of benzol-containing gas are passed the composition of the issuing vapour will show differences from the original, the lighter fractions being displaced in accordance with the general rule that from a mixture of substances of similar constitution charcoal preferentially adsorbs those of higher molecular weight. The break-point can be determined dynamically by passing the gas-vapour mixture under examination through a tube packed with the charcoal, and examining the issuing gas in a Haber-Lowe gas interferometer. The values obtained are, of course, influenced by the packing and length of the charcoal column and the rate of flow of gas, and the method is best suited for comparative purposes.

At low partial pressures of vapour the determination of the adsorption isotherm is likely to be a difficult and lengthy operation. Allmand and Manning [1] have introduced a simpler and more rapid method of calculating the isotherm from the desorption curve and the retentivity. This latter quantity was introduced by Chaney,[2] and was determined by him as follows.

A specimen of the charcoal is dried, evacuated, and saturated at 22° with the vapour in question at a definite partial pressure. The charcoal is weighed and then evacuated at 2 mm. pressure at 100°, being re-weighed every half-hour. The relative weights of vapour retained are plotted against time and when three successive readings lie on a straight line the curve is produced back to the $\frac{X}{m}$ axis. The intercept on this axis is defined as the retentivity of the charcoal.

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[1] *J. Soc. Chem. Ind.*, 1928, *47*, 370T. [2] *Ind. Eng. Chem.*, **1923**, *15*, **1244**.

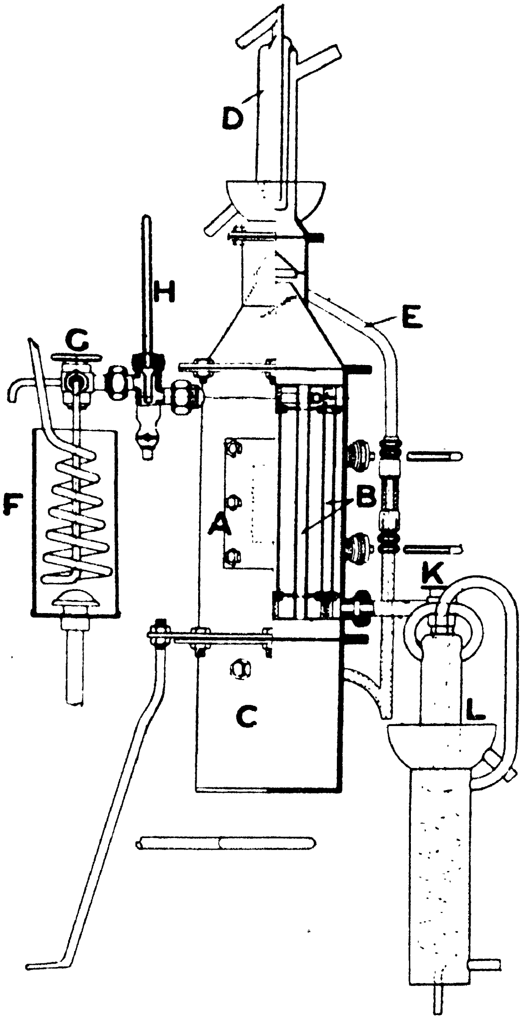

FIG. 4 (XIII[3])
Charcoal testing plant

Allmand and Manning modified this concept of retentivity by carrying out desorption in a constant stream of air at 100°. At this temperature equilibrium is set up so quickly between the sorbed and vapour phases that the form of the desorption curve is independent of the rate of air flow within fairly wide limits, and consequently no allowance need be made for the varying times of contact with equal weights of charcoals of different density. The air-stream is interrupted every 10 minutes and the tube weighed. From the graph of $\frac{X}{m}$ against litres of air passed, the adsorption isotherm can be calculated by finding the slope of the tangents at different values of $\frac{X}{m}$.

Voss[1] describes an apparatus for testing charcoals on a pilot plant scale, which permits of steaming-out the charcoal. The extractor is shown in Fig. 4 (XIII^3), in exterior and sectional elevation. It consists essentially of a charcoal filter A fitted with a manhole for charging. Through the filter passes a number of heating-tubes B which connect directly with a boiler C and a double-surface condenser D. When the charcoal has been saturated by passage of gas and it is desired to distil off the sorbate, the burner is lit under the boiler C, which contains aniline, or other liquid of suitable boiling-point, and the gaseous aniline passing up the tubes effects a rapid heating of the charcoal bed. The aniline condenses in the double-surface condenser D at the top of the apparatus and returns to the boiler by the return pipe E, which is fitted with a sight-glass to enable the operator to determine the commencement of the distillation and to regulate it. At the same time steam, superheated in the superheater F, is allowed to enter by the three-way tap G and a distributing-ring at the top of the filter. The temperature of the steam entering the charcoal is recorded by the thermometer H. Solvent vapour and steam pass out through the two-way tap K and are condensed in the condenser L. This specially designed condenser is a combination of a double-surface and a spiral condenser, and effects very efficient cooling at comparatively rapid rates of distillation.

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[1] *J. Soc. Chem. Ind.*, 1930, *49*, 343T.

SECTION 3: ACTIVATED CARBON

Activated Carbon. Processes for activating charcoals fall into two distinct classes, in each of which certain special methods have become standardized. In chemical methods of activation the raw material is impregnated with various substances—zinc chloride and syrupy phosphoric acid are widely used—before carbonization. When zinc chloride is employed the carbonization temperature lies between 400° and 800°, and the zinc oxide remaining is leached out with acid; H_3PO_4-treated [1] materials on the other hand are given an 8–10 hour carbonization at a final temperature of approximately 1,000°. The acid is reduced, phosphorus distils off, and may be re-oxidized to the acid.[2]

In the second, more flexible and perhaps more widely used method, activation is effected by the oxidizing action of air, steam, or flue gases at high temperatures on the primary carbon, which must have been liberated at a temperature not exceeding 600°–700°. In general, the activity of the product increases with time of steaming and at the expense of the yield and the bulk density.

Quite different from either of these is Radbruch's method [3] of obtaining a decolorizing carbon from peat by treatment with warm concentrated sulphuric acid. Activated carbon is considered to owe its increased activity compared with ordinary carbon to the hindrance of the formation of a surface layer on the charcoal from the decomposition products of the organic substance. The activity of the resulting carbon can be varied within wide limits by alterations in the organic substance employed, in the kind and amount of the activators and in the duration and temperature of the process.

Active charcoal consists essentially of amorphous carbon with varying amounts of ash. As the name implies it possesses to a greater degree the adsorbent properties of ordinary untreated charcoals.

It is generally used in the form of extruded pellets or of granules or fine powder and may be divided into two classes:

(1) The gas-activated type
(2) The chemically activated type

The manner in which activity varies with sorbate concentration or partial pressure is different for each type. Gas-activated charcoals are particularly efficient at low pressures, while chemically activated charcoals, in general, are not so efficient. The raw materials most commonly employed are peat, wood, and coal. High-temperature gas cokes cannot be activated to any useful extent.[4] The different processes used involve at some stage or other (*a*) the production of porous, amorphous carbon, (*b*) the activation or surface cleaning of this carbon. For type (1) the raw materials are first carbonized at temperatures differing for different materials. The product is then crushed and screened to a suitable size and charged into a retort where it is treated with steam or steam and air at a certain temperature. (The temperatures differ in different processes.)

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[1] This notation is employed throughout in the interests of brevity.

[2] Reilly and O'Donoghue, *Sci. Proc. Roy. Dub. Soc.*, 1941, *22*, 367.

[3] *Z. angew. Chem.*, 1939, p. 590.

[4] *Full Research Technical Paper*, No. 47.

Chaney [1] has placed the temperature of low carbonization at 600°. It appears that at high temperatures the carbon is changed to graphite and then does not react so readily with steam. According to Lamb, Wilson, and Chaney [2] activity is due simply to the increase in porosity and internal surface brought about by the activating gas. Hydrocarbons produced during carbonization and strongly adsorbed by the carbon atoms are partly oxidized in activation so that the adsorptive forces are released. Much external combustion occurs at the same time, which explains in part the low yields obtained in these processes. Steam activation is commonly employed at 850°–950°. Air is effective even as low as 350° but the reaction being exothermic is difficult to control. The products are more friable than those obtained with steam. Mixtures of air and steam [3] and of steam and carbon dioxide are also employed. Oxygen (6 per cent) with steam reduces the activation temperature to 500°–600°, which is maintained by the heat of reaction.[4] Sulphur vapour and combustion gases with or without added air are also used.[5]

Few raw materials have the necessary density and structure for direct conversion into active charcoal. The employment of briquetting in manufacturing greatly widens the choice of raw materials and at the same time increases the yield and hardness of the products obtained therefrom. The raw materials may be briquetted under pressure and then carbonized and then activated. More often they are agglomerated after carbonization with a binder such as pitch, tar, petroleum oils, &c., then when subdivided, and recarbonized, they are finally activated. Different raw materials may be blended by this method. Norit is a steam-activated briquetted charcoal.[6]

The impregnation of carbonaceous materials with compounds such as the chlorides of zinc, calcium, magnesium, &c., alkalis, sulphuric acid and phosphoric acid affords a means of producing high yields of charcoal at relatively low temperatures which require but little subsequent activation. The action of the reagents appears to be one of dehydration with direct liberation of carbon unaccompanied by the tarry materials of pyrogenation. Processes based on this method involve grinding of the raw materials and extrusion under pressure of the pastes formed with the reagents so that the advantages of briquetting already mentioned are thereby included. The products are of a special type. The process of chemical activation as now commonly practised was due to R. Ostrejko,[7] who sought to produce a highly active decolorizing charcoal. Zinc-chloride-activated charcoal cannot be regenerated after use, but air- and steam-activated charcoals can be reactivated by a repetition of the activation process. A modification of active carbon (prepared by treating active carbon with sulphuric acid, chlorine or active oxygen) is used to remove salts, colours, &c., from aqueous solutions. The temperatures for activation of charcoal may range from 350° to 1,150°. In the preparation of active carbon the important factors are both cell size and continuity. Lowry and Hulett[1] have shown the mean capillary diameters of active charcoals to be of approximately molecular size ($2{\cdot}8$ to $9{\cdot}2 \times 10^{-7}$ cm.), while the upper limit of 0·012 mm. for efficient adsorption of vapour has been given by Harkins and Ewing.[2] The briquetting of a pulverized coal blend is a means of ensuring this structure, provided that the blend is balanced so that plasticity on carbonization is not achieved, and a secondary structure is not formed by the escape of volatile matter. In the absence of plasticity the particles of coal may become in themselves porous.

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[1] U.S.P. 1499908.

[2] *Ind. Eng. Chem.*, 1919, *11*, 420.

[3] *Fuel Research Technical Paper*, No. 47.

[4] B.P. 357778, 1930.

[5] B.P. 224521, 1924; 270505, 1926.

[6] B.P. 198328 and 206862, 1923; 228954 and 247241, 1924.

[7] B.P. 14224, 1900.

The outstanding property of active charcoals is their adsorptive activity towards vapours, gases, and dissolved substances. All known gases are adsorbed to a greater or lesser extent. Activity is expressed in terms of adsorptive capacity which is measured for any given substance by the quantity adsorbed under specified conditions of temperature and pressure. The following figures[3] serve to show the order of activity of coconut charcoal towards organic and inorganic vapours. The data were obtained at saturation pressure and 0° and are as follows :

Carbon tetrachloride	71·0 per cent
Carbon bisulphide	58·1 ,, ,,
Benzene	41·9 ,, ,,
Ether	36·2 ,, ,,

Adsorption of Gases by Charcoal. 1 ml. box charcoal at 12° and 724 mm. adsorbs ammonia 90 ml., 65 ml. of sulphur dioxide and 55 ml. of sulphuretted hydrogen. Coconut charcoal adsorbs about 200 times its own volume of ammonia at N.T.P.

Hydrogen cyanide and water-vapour are exceptional. Studying a group of charcoals Allmand and Chaplin[4] found a maximum adsorbability of about 0·5 per cent at 0·2 mm. and 25°. In general the higher the molecular weight of a compound the greater will be its adsorbability, but quantitative relations exist only in the case of organic compounds of the same class.

Adsorptive capacity increases with pressure and decreases with temperature for most substances (*cf.* the solution of gases in liquids). The pressure/quantity relationship at constant temperature being given by the adsorption isothermal. Numerous data showing these relationships for various substances and for different charcoals have been collected by McBain.[5] A review of adsorption equations has been made by Swan and Urquhart.[6] A well-known equation relating quantity adsorbed (x/m) and pressure (p) or concentration (c) is : $x/m = \mathrm{K}p^{\frac{1}{n}}$ or $\mathrm{K}c^{\frac{1}{n}}$, where x is the quantity of substance adsorbed by *m* of charcoal and K and *n* are constants characteristic of substance and temperature. This relationship has a wide applicability. No single equation, however, applies accurately over the whole known pressure range. In the low-pressure region charcoals differ markedly in activity. Vapour adsorbed at pressures represented by the steep part of the isotherm is easily removable from the charcoal, but that adsorbed prior to this is not. A measure of the retentive power is known as the retentivity of the charcoal, which is usually determined for a given vapour by streaming dry air or nitrogen through the charged charcoal at 25°, 100° or 130° until the rate of loss becomes insignificant. According to Chaney, Ray, and St. John [1] the retentivity for vapours is proportional to its adsorptive capacity for non-condensable gases and to its decolorizing power for liquids. These properties are all manifestations of adsorption on active surface (chemical forces) as distinct from condensation in capillaries (physical forces). Steam-activated nut and briquetted charcoals in general have a high retentivity. Chemical-activated charcoals have low retentivity but high capacity for vapours at moderate partial pressures.

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[1] *J. Amer. Chem. Soc.*, 1920, *42*, 1393.

[2] *Ibid.*, 1921, *43*, 1787.

[3] Coolidge, *J. Amer. Chem. Soc.*, 1924, *46*, 596.

[4] *Proc. Roy. Soc. A.*, 1931, *132*, 460.

[5] *The Sorption of Vapours and Gases by Solids*, 1932, p. 58.

[6] *J. Phys. Chem.*, 1927, *31*, 251.

The velocity of adsorption as measured *in vacuo* is very high for all but the final stages of adsorption. From a practical point of view it is practically instantaneous.[2] At high vapour concentrations a short interval is allowed to facilitate dissipation of the heat of adsorption and so avoid unduly raising the temperature of the charcoal. The velocity of adsorption from solution is low in comparison with that observed in the gaseous phase, being dependent on the rate of liquid diffusion. In general, times of contact 50 to 100 times as long as those for adsorption from the gaseous phase have to be employed, and liquids to be treated are either filtered at low rates through beds of active charcoal or heated and agitated for definite times with a sufficient quantity of the adsorbent in a finely divided state.

The utility of active carbon for the production of high vacua was first pointed out by Dewar,[3] who observed the great increase in adsorptive capacity which resulted from cooling charcoal to low temperatures. Coconut charcoal, being the most retentive, is generally used. The charcoal is first evacuated at elevated temperature to a pressure of the order 10^{-2} mm. after which it is cooled in liquid air and put into communication by means of a tap with the apparatus to be evacuated. Under proper conditions it is possible to reduce the pressure to 10^{-5} mm. in a few hours.[4]

Activated carbon is also employed in the estimation of hydrocarbons in gases. For the recovery of hydrocarbons from coal or other gas in amounts suitable for analysis a convenient apparatus has been described.[5] Active charcoal is also a most efficient medium for the thorough purification of gases from oil vapours. To dry them thoroughly pass over silica gel. In assessing the value of active carbon for any given purpose it is important to test it under the conditions in which it is required to be used.

A few industrial applications may be quoted : recovery of valuable products which exist as attenuated vapours in unadsorbable gases, e.g. C_6H_6

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[1] *Ind. Eng. Chem.*, 1923, *15*, 1252.

[2] *Proc. Roy. Inst.*, 1937, *18*, 750.

[3] B.P. 13638, 1904.

[4] Kaye, *High Vacua*, 1927.

[5] Hollings, Pexton, and Chaplin. *Trans. Inst. Chem. Eng. Anal.*, 1929, 7, 102; *see also* Voss, *J. Soc. Chem. Ind.*, 1930, *49*, 343T.

in coal gas. It is also used in gasolene recovery. It can be employed to remove phenol from effluent gasworks liquor, or for removal of sulphuretted hydrogen from town's gas and recovery of sulphur therefrom. In this it also acts as a catalyst. Other uses include the purification of drinking water, sugar decolorizing, for respirators, for maintenance of a vacuum in the jackets of commercial containers for liquid air and to facilitate chlorination of organic substances.

Measurement of Activity. The estimation of the true activity of a charcoal is very difficult; the order of activity of two carbons may be reversed in different solutions, and two carbons which have the same adsorptive efficiency at a given concentration of sorbate may differ widely in performance at other concentrations. In the examination of charcoals from peat by Reilly and O'Donoghue[1] the following procedure was adopted. The charcoals were submitted to three tests, in every case in comparison with commercial standards:

(i) Bulk density of 180–270 mesh fraction. This is of value as affording a measure of the porosity of the charcoal.
(ii) Determination of the phenol isotherm.
(iii) Determination of the decolorizing power towards dilute solutions of molasses.

The peat samples were activated in different ways, using zinc chloride, steam, phosphoric acid, and sulphuric acid. Since activation with warm concentrated sulphuric acid differs radically from other methods of activation, it is considered separately. Three lots were activated by this method. The raw material in all cases was ground till more than 80 per cent of it passed a 30-mesh screen, and dried again before adding to the concentrated acid, which was contained in a beaker in an oil-bath. Frequent stirring with a thermometer is necessary to prevent local overheating of the pasty mass produced. The addition of the peat to the acid causes a sharp rise in temperature, accompanied by evolution of sulphur dioxide, which continues to come off during the whole of the heating period. When heating was finished the beaker was emptied into a large quantity of cold water, and the product washed by decantation and with hot water at the pump till free of sulphate. It was then dried, ground till all passed a 180-mesh screen, and dried again for 2 to 3 hours at 110°–120°.

In all cases the name of the primary substance is given first, then follows the maximum temperature of treatment, and finally the number of minutes for which this temperature was held. E.g. a-$ZnCl_2$/450°/60 denotes the charcoal obtained when the a-$ZnCl_2$-treated residue was held at 450° for 60 minutes. Similarly PC/SA 800°/30 means primary charcoal, steam activated at 800° for 30 minutes.

Preparation of the Starting Materials.—*a*-$ZnCl_2$. 300 grams of dried residue was added to a solution of 120 grams anhydrous zinc chloride in 400 ml. water plus a few drops of hydrochloric acid. After thorough mixing the damp mass was dried on a tray for 2 days at 30°, and finally at 100°, to give a very friable product. The yield was 94 per cent of the weight of residue and zinc chloride used.

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[1] *Sci. Proc. Roy. Dub. Soc.*, 1941, *22*, 367.

b-$ZnCl_2$. Here only 60 grams zinc chloride was used for 300 grams residue, otherwise the treatment was the same as the above. The yield, calculated as above, was 93 per cent.

In both cases there was no appreciable heat evolution on mixing, and no change of note in the appearance of the residue.

a-H_3PO_4. 300 grams residue, ground till more than 80 per cent of it passed 30 mesh, and dried, was added to 300 ml. of concentrated phosphoric acid (sp. gr. = 1·75) and mixed thoroughly in a shallow dish to form a dark pasty mass. After drying for 2 days at 100°–120° the product was brownish-black, dry, and much of it in fairly hard lumps. The yield was 84 per cent of the weight of residue and phosphoric acid taken.

b-H_3PO_4. Here the quantity of phosphoric acid used was only half that employed in the *a*-H_3PO_4 treatment; in other respects conditions were practically identical. After drying, however, there was no loss in weight and no formation of lumps.

Preparation of Primary Charcoal. The preliminary carbonization of that part of the first batch of residue intended for steam activation later was carried out in the furnace of Reilly and Donnelly.[1] For various reasons the temperature was not regulated very accurately, though the point is probably of minor importance. All lots, however, were treated somewhat as follows: 2 to 3 hours' heating in a current of coal gas to 400°, then kept at 400°–420° for 2–3 hours longer, still with gas passing. Carbonization appeared to be complete after this length of time, the average yield being 46 ± 2 per cent on the weight of dried residue in the charge. The separate lots were mixed thoroughly before storing in tightly closed tins.

The Furnace was used for the heat treatment of all but the primary charcoal; it resembles somewhat the retort used by Ardagh.[2] A 12-in. length of 3-in. steam-pipe was closed at one end by a welded-on stop, at the other by a flange to which a circular cover-plate could be bolted, the joint being made gas-tight with an asbestos washer. Short lengths of ¼-in. pipe served as inlet and outlet, and in addition the small end was fitted with a short sleeve to carry the thermocouple (Fig. 5 (XIII³)).

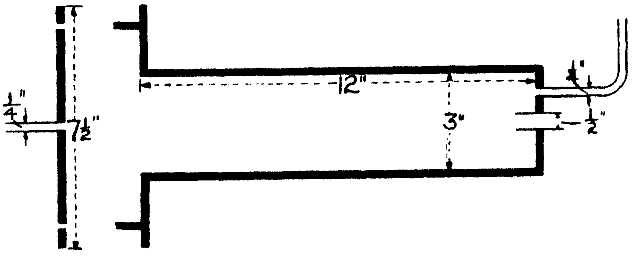

FIG. 5 (XIII³)
Carbonising retort

A length of 4-in. asbestos piping enclosing the retort carried the electrical winding. This was in two sections, each covering half the furnace chamber and consisting of about 70 ft. of No. 19 S.W.G. 80/20 nichrome wire, crowded together somewhat at the outer ends to compensate for increased radiation losses there. After winding, the retort was enclosed in a sheet steel drum 9 in. in diameter, packed with asbestos. The ends were likewise heavily lagged. The leads were brought to three terminals on the outside of the furnace, and so arranged that the windings could be put either in series or parallel as desired.

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[1] *Sci. Proc. Roy. Dub. Soc.*, 1930, *19*, 29.

[2] *J. Soc. Chem. Ind.*, 1921, p. 230T.

Two external series resistances, one coarse and one fine, served to control the furnace temperature. The thermocouple used to measure this was a platinum—platinum-iridium type used in conjunction with a millivoltmeter reading to within 5°. The hot junction was at the centre of the chamber, but, in any case tested, no temperature gradient along the furnace could be detected.

The asbestos pipe as a core for the windings was adopted after the mica first tried had broken down. Its strength, convenience, and ability to withstand high temperatures without breakdown go far to outweigh its poor thermal conductivity.

Preparation of Charcoals. Irrespective of origin, all carbons prepared were treated as follows: Crude charcoal from carbonization acid-extracted by standing in warm, moderately dilute hydrochloric acid for 1 or 2 days. Then filtered, and washed with hot water at the pump till no excess chloride could be detected in the runnings. Dried and ground in a mortar till all passed 180 mesh. Finally dried at 100°–120° for 2 to 3 hours and bottled.

The duration of heating varied with the material being carbonized; for example, $ZnCl_2$-treated batches got 1–1½ hours' pre-heating before being held at the desired temperature for 1 hour, while H_3PO_4-treated residue was carbonized for 8–9 hours with the temperature rising steadily to the maximum, at which it was held for 30 minutes. In all cases where tar was being evolved a slow current of coal gas was maintained through the furnace till heating had ceased.

Steam Activation. The activating effect of steam is due most probably to its oxidizing action on tarry hydrocarbons fouling the carbon surface. The main reaction $C + H_2O \rightleftharpoons CO + H_2$ in this oxidation is affected by time, temperature, rate of steam flow, accessibility of steam to carbon, and other factors. Good circulation of steam is of obvious importance, but the industrial methods of securing it (rotating the retort, &c.) are not easy to reproduce on a small scale. The rate of steam flow is more important at temperatures above about 850°, when equilibrium is rapidly attained and an inadequate steam flow may slow up the activation considerably. We do not know of any published work on the effect of grain size on activation, but obviously the interior of a large granule cannot—even allowing for diffusion—be as well activated as the surface. This less activated carbon will form the coarser fraction in grinding, and consequently one may expect that the bulk density of such a char will be disproportionately high.

Experiment justified all these conclusions. In the earlier experiments (30-minute chars) the ungraded primary charcoal was loaded to a depth of 3–4 mm. on two flat steel trays inserted in the furnace. Though the steam flow was kept roughly constant, and gas circulation over both trays was unhindered, the position of the steam inlet obviously favoured the upper tray, and a much greater percentage of the carbon on it was gasified, especially at higher temperatures.

In an effort to secure better exposure of charcoal to steam, the primary carbon for the 60-minute activation was screened, and the fraction on the 10-mesh used, loaded as before. The difference between the trays persisted, however, while the yield was, as might be expected from the lower ratio of surface to mass, greater.

In all cases the chars from the two trays were mixed before extracting with acid.

The superheater used in these experiments was an 18-in. length of ½-in. steam-pipe, heated in an ordinary laboratory combustion furnace. With a little experience the superheater temperature can be regulated fairly well, though some muffling is necessary when working at 950°.

Only the most significant features in a considerable amount of experimental data can be given here.

Percentage Yields. All the following are calculated as weight of finished charcoal on weight of dried residue taken. The figures for the steam-activated carbons should be considered in the light of the discussion earlier :

Charcoal	Per cent yield
H_2SO_4-activated carbons	70–75 per cent
$ZnCl_2$-treated charcoals	53–63 ,, ,,
H_3PO_4-treated charcoals	50–55 ,, ,,
Steam-activated charcoals	13–21 ,, ,,

Bulk Densities. These were determined by taking 7–10 c.c. of the 180–270 mesh fraction of each charcoal and tapping it down to constant volume in a 10-c.c. measuring cylinder of about 1 cm. diameter. The bulk densities varied between 0·400 and 0·762.

Chaney[1] quotes values from 0·216 to 0·548 for 200–270 mesh fractions of activated charcoals from various sources.

Phenol Isotherms. 1 gram of each charcoal was weighed into small stoppered conical flasks, and distilled water and then phenol (kept as an aqueous solution in a hydrogen atmosphere) added to make a total volume of 20 ml. After mechanical shaking for 30 minutes each batch of flasks was filtered and the residual phenol in 10 ml. estimated by titration. The data so obtained were plotted according to the logarithmic form of the adsorption isotherm :

$$\log \frac{100x}{m} = \log k + \frac{1}{n} \log C.$$

Molasses Decolorization. A filtered solution of molasses was diluted till the colour was brought into a fixed relation with a permanent standard. The specific gravity was 1·01, and the colour fairly dark.

In carrying out the tests the fresh solution was run into conical flasks containing appropriate weighed amounts of the various carbons. These were kept at 50°–60° in an air oven for 30 minutes with occasional shaking, then filtered and the filtrate poured back once over the paper. The percentage colour remaining was found in a Klett colorimeter, using appropriate sub-standards.

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[1] *J. Ind. Eng. Chem.*, 1923, *15*, 1252.

Fig. 6 (XIII[3]) is a specimen of the type of graph obtained for phenol isotherms in the examination of various treated charcoals. A highly active carbon was included for comparison. Similar comparisons were made for molasses decolorization.

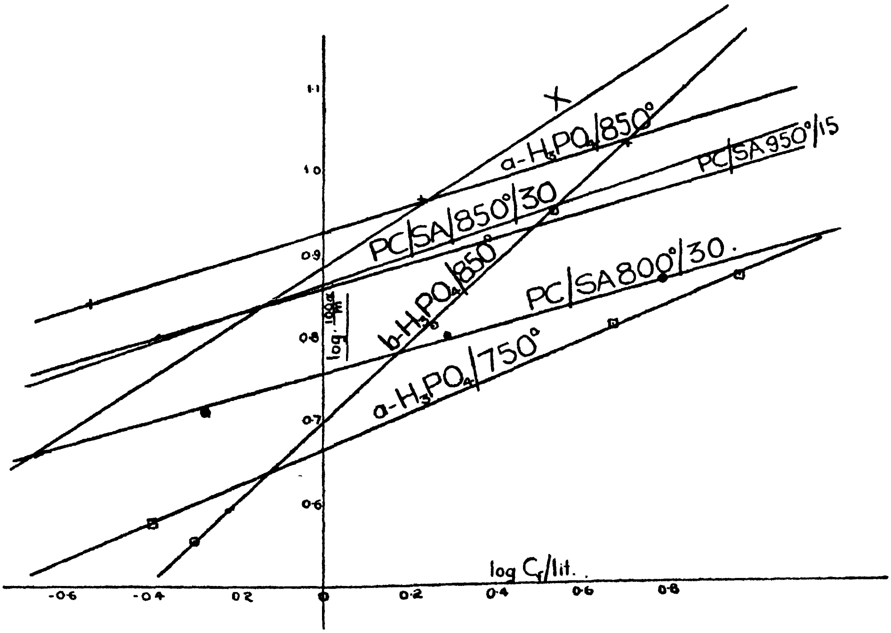

FIG. 6 (XIII[3])
Phenol isotherms with charcoals prepared in various ways

Variations in Amorphous Carbon. According to Riley,[1] amorphous carbons are built up from two types of structure, viz. (i) the turbostratic lamellar, graphite-like structure, and (ii) the disordered, three-dimensionally cross-linked structure. Amorphous carbons which contain a preponderance of structure (i) are usually much purer than those made up largely of (ii): it is possible that the foreign atoms, hydrogen together with oxygen, nitrogen, or sulphur play some part in stabilizing the type (ii) disordered structure.

Such a view of the crystallographic character of amorphous carbon, it is claimed, appears to offer a reasonable basis for the explanation of the great diversity of its properties, the great variation in its chemical reactivity, the differences in its mechanical properties and scattering power for X-rays, &c. Carbons deposited from the gas phase, which may contain little or no combined oxygen, will be made up largely of type (i) structures, whilst chars and cokes in general will consist of intimate associations of both types.

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[1] *Quarterly Review*, Chem. Soc., London, 1947, —, 59.

SECTION 4 : ADSORPTION AND FILM LAYER SURFACES

Measurement of specific surface areas from particle size-weight distribution by air-elutriation and liquid-sedimentation methods have been made. Low-temperature adsorption methods have also been utilized to obtain surface measurements. *See* Vol II, Chap. I, p. 20.

In connexion with the experimental investigation of the adsorption isotherms, e.g. nitrogen and *n*-butane at pressures above the gas region, the apparatus of Emmett and Brunauer [1] has been used by Jura and Harkins.[2] For the determination of adsorption at pressures below 100 mm. they used a different type of apparatus. It is shown in Fig. 7 (XIII³). The bulb B contains the adsorbent, while R, which holds the liquid whose vapour is to be adsorbed, may also be used as a gas reservoir if it is desired to investigate

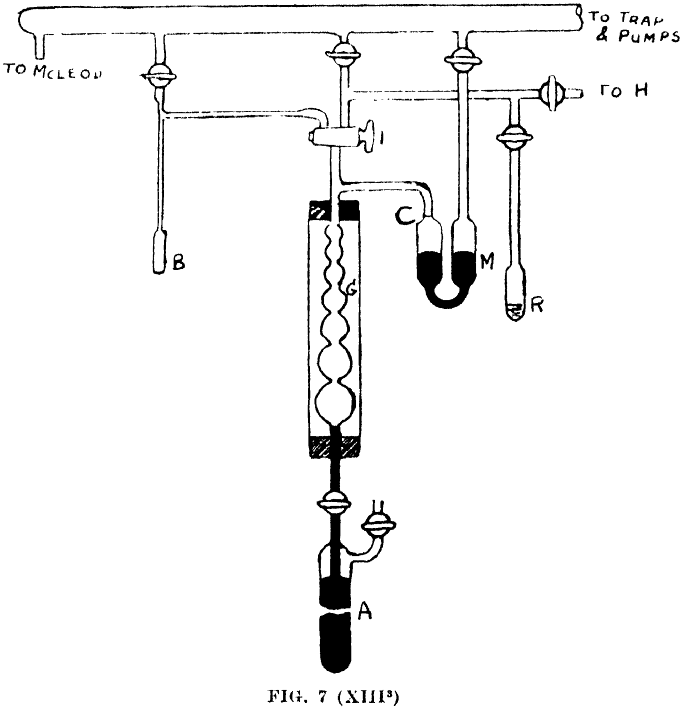

FIG. 7 (XIII³)
The apparatus of Emmett and Brunauer for the investigation of adsorption isotherms

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[1] *J. Amer. Chem. Soc.*, 1934, *56*, 35.

[2] *Ibid.*, 1944, *66*, 1358.

only the very low-pressure region of the isotherm. The mercury manometer M is made of 25-mm. tubing, since the diameter should be large in order to allow the meniscus to move freely. A set of calibrated bulbs G is employed to control and measure the volume of the gas adsorbed. A mark C is used in the determination of the volume of that part of the manometer which is in the adsorbing system. Stop-cock 1, when open, permits the gas to enter the burette system and then to pass to the adsorption bulb. The volume of the bulbs in G is determined by the weight of the mercury they hold. The volume of the left side of the manometer was determined as a function of the distance from the calibration mark to the level of the meniscus, and the volume of the tubing leading from the graduated bulbs was obtained by measuring the change in pressure as the volume in the bulbs is decreased by successively filling them with mercury from the reservoir A. For one system used by Jura and Harkins the volume of the tubing was 25·10 ml. The average deviation was 0·02 ml. or less than 0·1 per cent. The dead-space in the adsorption-chamber was determined with helium by measuring the initial volume and pressure in the burette system, and also the final pressure after the gas had been allowed to expand into the dead-space. The difference in height of the mercury in the arms of the manometer was determined with a travelling-microscope of a sensitivity of 0·001 mm., which was set on a transit mount so that it could be rotated. The average deviation of a given height when a series of readings were taken was found to be 0·002 to 0·003 mm., while that of a single reading from the average did not exceed 0·006 mm. The screw of the microscope was not in error by more than 0·010 mm. and its errors are known to 0·001 mm. After the surface of the sample has been degassed, the dead-space determined, and the sample placed in the thermostat, the helium is pumped out, and successive additions of vapour are made. The initial and final volume and pressure of the vapour are measured, and the amount adsorbed is calculated from the gas laws.

The Determination of the Effective Areas of Film-forming Molecules. A rapid and convenient method for measuring the effective areas of polar molecules at a film pressure of 10·3 ± 0·3 dynes per cm. is described by Miller.[1] It is based on the equilibrium of tensions which is established at the point where the monolayer has developed a pressure large enough to prevent the spreading of a lens of the substance on the substrate. This film pressure for a variety of polar substances dissolved in pure benzene at concentrations of 0·5 to 2 × 10^{-6} gram-molecules per ml. is 10·3 ± 0·3 dynes per cm. The method which does not require the use of a surface balance consists in determining the exact amount of benzene solution required in order to form the first stable lens on a substrate of known area. At this point the surface is covered with a monolayer at a film pressure of 10·3 ± 0·3 dynes per cm. The equilibrium established at the lens end-point is not reversible ; in the presence of excess of the solution the equilibrium shifts towards the development of higher film pressures, the increase in film pressure being accompanied by an increase in the lens angle. Measurements of lens angles and film tensions corresponding to the lens end-point have been found to satisfy equations derived by applying

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[1] *J. Phys. Chem.* 1941, *45*, 289.

Neumann's theorem to the systems—for the theoretical treatment Miller's paper should be consulted.

The Apparatus. A 0·1 ml. serological pipette and a glass photographic tray are used. The tray contains the substrate, either water or dilute acid, and must be well illuminated. The solution of film-forming substance is added drop by drop to the surface of the substrate from the pipette. The first drop spreads rapidly ; subsequently the drops spread more slowly and at this point the solution is added in 0·002 ml. portions by allowing this amount to flow out on the end of the pipette and touching this to the water surface. The end-point is reached when the addition of a 0·002 ml. portion produces a stable lens on the surface of the substrate. This one is the first one which is in equilibrium with the film and may be called the 'equilibrium lens'. The equilibrium lens may be distinguished from all preceding lenses by the following six criteria :

1. The first drops added to the surface form relatively short-lived lenses. The equilibrium lens remains on the surface for appreciable periods of time which depend on the temperature of the substrate.

2. The shadows of lenses just prior to the equilibrium lens are surrounded by dark haloes. These haloes are easily observed if the lens system is located directly below a ceiling light and a bright metallic surface is placed beneath the glass tray. As the equilibrium lens is approached the halo moves inwards until it disappears entirely for the equilibrium lens.

3. The equilibrium lens is definitely circular in outline and has a sharp boundary. Previous lenses have boundaries of definite widths, which occasionally show interference fringes or give reflected sparkles which indicate that the lens edge is vibrating.

4. Light is focused sharply by the equilibrium lens to form a small bright spot on the bottom of the tray. Previous lenses are incapable of giving a sharp focus to the light, since they are not truly lenticular. With some systems the focal length of the equilibrium lens is too long to give a sharp point of light on the tray. The fact that these lenses are truly lenticular may be shown by placing a sheet of graph paper beneath the glass tray and observing the characteristic magnified spacings produced.

5. The first lenses added to the substrate move more or less rapidly over the surface since the surface tension of the substrate is reduced unevenly around them. The equilibrium lens remains relatively quiescent, since the formation of the complete film has established an equilibrium of tensions (with some systems the completion of the film seems to be accompanied by a relatively large increase in surface viscosity, which entirely stops the motion of the lens).

6. If two lenses are placed near to each other they are unstable in each other's presence if they are not equilibrium lenses. One lens (or both) will vibrate violently and assume a very irregular outline. Streamers of liquid will leave from between the two lenses in a fan-like sheaf. These lenses never merge together. However, at the equilibrium-point, two lenses may be put very near together without showing any effect upon each other. Both will remain perfectly circular in outline, give sharp foci of light and remain relatively quiescent or slowly merge together.

The effective area of the polar molecules is given by the equation

$$X = \frac{A \times 10^{16}}{V \times C \times 6{\cdot}06 \times 10^{23}}$$

where X = effective area of molecule
A = surface area of substrate in sq. cm.
V = vol. of solution used in ml.
C = concentration of solution in gram-mol. per ml.

Before making a measurement the glass tray is washed with warm acid dichromate and rinsed with distilled water. The surface of the substrate is cleaned by laying thereon a large sheet of filter-paper, and when this has become wet through, drawing it by means of the dry edge right across the tray at least twice.

The pipette is calibrated with mercury and is cleaned before each filling by means of pure benzene which is removed by evacuation. After filling any excess of solution on the outside of the tip is removed with filter-paper. The results obtained agree within 3 per cent with those obtained with the film balance method.

CHAPTER XIV [3]

CHROMATOGRAPHY [1]

WHEN a solution containing one or more coloured substances is percolated through a column of suitable adsorbent, partition occurs between the adsorbent and the solution : the adsorption coefficient and the concentration being the determining factors. When the solution first comes in contact with the adsorbent, in the topmost layers, some of each of the solutes will be adsorbed, but soon the less strongly adsorbed compound will be displaced by the most strongly adsorbed which alone is removed from the solution. That this displacement does occur can be shown experimentally : if we have a solution containing a red and a yellow dye, and on percolation the red is found to be stopped at the head of the column and the yellow passes farther down, we see that the red is more strongly adsorbed. Now if a solution of a yellow dye is poured on to the column a yellow layer forms at the top ; when the red dye solution is added the yellow layer will move farther down the column and its place will be taken by the red. If the red solution is first to be added it will form a layer at the top and the subsequent addition of the yellow will not displace it : instead a yellow layer will be formed as before.

Consideration will show that the repetition of the process will result in all the most strongly adsorbed substance being removed from the solution and concentrated in the top layer. In the next layer below the same mechanism will result in the deposition of all the next most strongly adsorbed solute. By this means the different substances are collected in successive layers. If the substances are coloured these layers can be seen and separated from one another. The distinctness of separation of the layers can generally be much improved by percolating the column with the pure solvent : this is called ‘ developing ’ the chromatogram and often results in the formation of well-defined empty (of colour) bands between the adsorbed layers. Such a result obviously is very valuable when the zones are separated, in order that the individual substances may be eluted.

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[1] The original draft of a new section on chromatography revised from the 4th edition of *Physico-Chemical Methods* has been recast and expanded to its present size as a chapter by Mr. L. Devlin, University College, Cork. He has added a number of new facts, including the theory of the process.

SECTION 1: GENERAL PROCEDURE

The general procedure may be summarized as follows:
(*a*) Preparation of the column
(*b*) Preparation and addition of solution
(*c*) Development of chromatogram
(*d*) Sub-division of the column into its component zones
(*e*) Elution of the separate zones

Due to the great variety of factors, e.g. adsorbents, solvents, eluates, the solution concentrations, design of column and of apparatus, &c., success depends to a great extent on the exercise of individual skill. Until more is known regarding the practical mechanism of adsorption—chromatographical analysis is in some respects an art as well as a science.

A simple form of adsorption tube is shown in Fig. 1 (XIV^{3}). *See* Vol. II, p. 204, for details of construction and working. A rapid and convenient method of filling chromatograph columns has been devised by Levy.[1] The adsorbent and solvent are placed in a separating-funnel fitted with an efficient link stirrer. This is rotated and the resulting slurry allowed to flow through the tap into the clean dry column. The adsorbent settles fairly rapidly under gravity and the process may be aided by gently tapping the tube. In this way, a packing free from air-bubbles and giving the desired even banding is obtained.

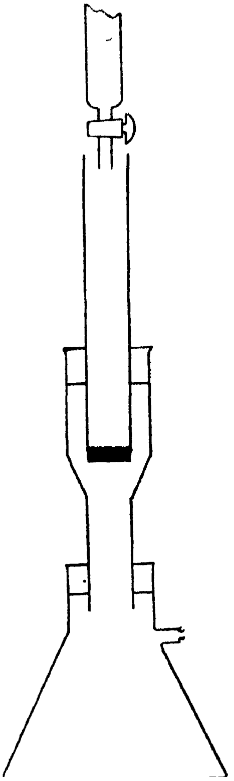

FIG. 1 (XIV^{3})
A simple form of adsorption tube. A plug of cotton wool fixes it in the centre of the cup-shaped funnel

General Chromatography and Applications. There are certain limitations to the method of chromatography. The substance to be chromatographed must not undergo chemical decomposition in the presence of the adsorbent (this may happen if an acidic solution is chromatographed on a basic adsorbent, and vice versa). In some cases the adsorbent catalyses the breakdown of the solute: for example, when certain azulene picrates are chromatographed, the aluminium oxide retains picric acid and the free azulene passes on.[2]

There is, however, a vast region in which chromatographical analysis can be used without difficulty. The problems may be summarized as follows:

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[1] *Chemistry and Industry,* 1945, *48,* 380.

[2] Plattner and Pfau, *Helv. chim. Acta.,* 1936, *19,* 858; *ibid.,* 1937, *20,* 224.

(i) Separation and isolation of the constituents of a mixture
(ii) Concentration of products in solutions of great dilution
(iii) Purification of substances
(iv) Establishing the identity of two substances
(v) Examination of a substance for contamination

The chromatographical behaviour of a substance is as characteristic as any other property (i.e. melting-point), and thus it furnishes an excellent method of identifying compounds, especially those which are coloured. The adsorption affinity of different compounds is in the order alcohols, ketones, esters, hydrocarbons, the last being least adsorbed : it also depends on the number of double bonds. Thus for the carotinoid alcohols the series commencing with the most adsorbed is Fucoxanthine ($C_{40}H_{56}O_6$) followed by violaxanthine, taraxanthine ($C_{40}H_{46}O_4$), flavoxanthine ($C_{40}H_{54}O_3$), zeathanthine and luteine ($C_{40}H_{35}O_2$).

(i) **Separation and Isolation of the Constituents of a Mixture.** Very small constitutional differences alter the adsorption affinity and so make separation possible. Some examples in which the method has been used are the separation of lycopin, α-, β-, and γ-carotin in which the proportions may be very different,[1] separation of α-, β-carotin by calcium oxide and calcium hydroxide,[2] separation of cis and trans isomers, e.g. crocetin.[3] For a descriptive example we may refer to Tswett's original experiment : on extracting green leaves with light petroleum and on percolating the extract through a column formed of compressed calcium carbonate, the contents of the solution underwent separation. At first, yellow, green, and yellow bands appeared ; when the picture was developed white interzones appeared separating the constituents as follows : in the upper part of the column a pale yellow ring appeared, immediately below it two green zones and farther down the tube three other separate yellow bands. The composite nature of chlorophyll was thus demonstrated. The method is extremely useful for the separation of the constituents of mixtures, because it can deal with such very small quantities, so small that attempts to separate them by fractional crystallization would be unsuccessful.

(ii) **Concentration of Products in Solutions of Great Dilution.** One of the most valuable applications has been in the concentration of natural products which occur in great dilution : very large volumes of the dilute solution can be passed through relatively small columns, the whole of the adsorbed material is eluted and the filtrate rejected, thus a great saving of time that would be necessary to evaporate off the solvent. Uropterin, a yellow pigment occurring in human urine at a dilution of 1 : 1,000,000 was isolated by Koschara as follows : 5,000 litres of urine were collected in 75 litres of 25 per cent hydrochloric acid solution. The solution was stirred for 10 minutes in 200-litre lots with 4 kg. of ' bleach earth XXF ' (adsorbent). The mixture was then filtered and the adsorbate was eluted with 14 litres of 20 per cent aqueous pyridine solution. The eluates were collected, and since they now contained a greater percentage of the pigment, its isolation was possible.[1]

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[1] Kuhn and Brockmann, *Ber.*, 1933, *66*, 407.

[2] Karrer and Walker, *Helv. chim. Acta*, 1933, *16*, 641.

[3] Kuhn and Winterstein, *Ber.*, 1931, *64*, 326 ; 1933, *66*, 209.

(iii) **Purification of Substances.** The purification of substances can be effected either by separation in one zone of the column, or alternatively by the separation of the impurity on the column. Thus can enzymes, &c., and other indefinite plant and animal substances be purified. The procedure consists first in freeing the enzyme by rupture or destruction of the cell walls, by such methods as vacuum drying or treating with dehydrators (like alcohol or acetone), triturating with quartz sand and pressing out the juice, destroying the cell walls by plasmolysis or freezing. The liquid so obtained is digested with acids, alkalis, salt solutions, or glycerol ; it is then submitted to a preliminary purification by such methods as treating with kieselguhr and centrifuging, precipitating the enzyme with acetone or alcohol, and the removal of the salts by dialysis. Alcohol or acetone is usually added and then the adsorbent is stirred in the liquid for 10 minutes or more. The adsorbent is separated by centrifuging : the final process consists in lixivation by digestion and stirring for a long time ; water is used for this purpose. A change of reaction is sometimes advisable. Ammonia, sodium bicarbonate, disodium phosphate, or acetic acid are useful reagents in this connexion. One further example of the advantages of chromatography as a method of purification will be described Purification of Penicillin.

The mould penicillin notatum is grown on a modified Czapek-Dox medium (Raistrick *et al.*). The culture fluid is filtered from the mould and the filtrate cooled to 0°. By the addition of a phosphoric acid solution, a *p*H of 1·9 is attained. The solution is then shaken with an equal quantity of amyl acetate, and the penicillin passes from the aqueous medium into the organic solvent. The *p*H is now raised to 6·5 by the addition of dilute barium hydroxide, the penicillin now passes into the aqueous layer once more. The aqueous extract is again cooled to 0° and the *p*H adjusted to 1·9 by the addition of phosphoric acid. On shaking with ether the penicillin again returns to the organic solvent. This ethereal solution of the penicillin is chromatographed by percolation through a column filled with small pieces of pumice on which has been precipitated aluminium hydroxide. Four zones can thus be separated (Fig. 2 (XIV^3)), (1) a short length of brown colour, (2) a longer length of pale yellow colour, (3) a shorter orange-coloured length, followed by (4) a short dark-coloured layer. The first three bands are removed and eluted separately in a phosphate buffer solution of *p*H 7·0. The solution from zone (2) is cooled to 0°, the *p*H again lowered to 1·9, and again extracted with ether. This ethereal solution is re-chromatographed ; three bands being obtained. The longest and lightest is removed and eluted in a phosphate buffer of *p*H 7·0. From this solution the penicillin can be isolated. (The other bands can be worked up for extra penicillin.)

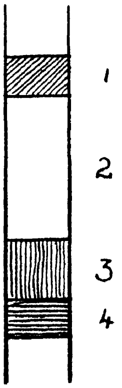

FIG. 2 (XIV^3) Chromatograph separation of penicillin

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[1] Koschara, *Z. physiol. Chem.*, 1936, *240*, 127.

(iv) **Establishing the Identity of two Substances** *and* (v) **Examination of a Pure Substance for Contamination.** The homogeneity of a substance and the identity or otherwise of two substances can be tested. If a solution of a substance is chromatographed and if there is no differentiation on the column, then the substance is homogeneous. Similarly if a solution of two substances together is chromatographed, the formation of two zones denotes non-identity and vice versa.

SECTION 2: COLOURLESS COMPOUNDS

So far the chromatography of coloured compounds has been discussed; the method, however, is no less valuable among colourless compounds. From time to time many and varied methods have been used to render the zones 'visible', the most satisfactory being summarized as follows:

(i) Many chromatograms fluoresce in ultra-violet light, making differentiation possible
(ii) Formation of coloured derivatives
(iii) Use of colour reactions as a means of rendering chromatograms visible
(iv) The empirical method

(i) **Fluorescence of Chromatograms in Ultra-violet Light.** In this case, the column may be contained in a quartz tube, examined and dissected under ultra-violet light which causes some of the compounds to fluoresce. Winterstein, Schon *et al.* were the pioneers of the ultra-chromatogram method. They isolated small quantities of anthraquinone from anthracene and showed that the chief impurity in this latter substance was identical with naphthacene.[1] 10 grams of anthracene Kahlbaum was adsorbed on a column of alumina (25 × 6 cm.). The column was developed with petroleum until half the anthracene passed into the filtrate. The adsorbent was then lixivated with a mixture of petroleum and methyl alcohol, the latter being later removed by shaking with water. The petroleum solution was again chromatographed and developed until half the anthracene had passed into the filtrate. The adsorbate was recovered from the adsorbent and percolated once more on a third column (8 × 4). The column was then examined in the ultra-violet light, five bands were recognizable (Fig. 3 (XIV^3)). 1 and 2 at the top of the column were two narrow yellow bands; these were followed by 3, a zone with a bright blue fluorescence, from which 5 mg. of carbazole were obtained as shining leaflets with a blue fluorescence. The fourth zone was a yellow band which contained the naphthacene, and following this was 5, a dark blue band from which anthraquinone was isolated. A concentration of 1/30,000 per cent of naphthacene suppresses the fluorescence of anthracene.

The spectro-chromatogram apparatus devised by Almasy [2] is illustrated in Fig. 4 (XIV^3). A is the slit of a quartz spectrograph, B is a quartz condensing lens, C a quartz chromatogram tube, and D a quartz mercury lamp shaded by a screen of Wood's glass, which only transmits radiations in the neighbourhood of 366 mμ. Almasy isolated benzpyrene from fractions obtained by the high vacuum fractionation of coal tar distillation residues. A solution of the fractions in hexane was chromatographed on alumina and developed with pure solvent until no more fluorescent substances pass into the filtrate. On viewing the column in the ultra-violet light, a number of fluorescing zones are visible. The column is then focused on the slit of the spectrograph, and by comparing with the fluorescence spectrogram of adsorbed benzpyrene, the required zone is easily located and identified.

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[1] *Z. physiol. Chem.*, 1934, *230*, 146; *Naturwiss.*, 1934, *22*, 237.
[2] *Biochem. Z.*, 1937, *291*, 425.

A separation of peat wax alcohols has been made possible by chromatographing means with subsequent examination of the column in the ultra-violet.[1] A tube 50 cm. long by 2·5 cm. diameter was packed with aluminium oxide (Brockmann). Alcohols from the esters in peat wax were dissolved in petroleum ether (B.P. 80° 90°), and allowed to percolate through the tube. The ' picture ' was developed by first washing with pure solvent, and then with petroleum ether containing 5 per cent alcohol—the bands were thus spread out. Four bands of colour were clearly identifiable, each a different intensity of yellow. The column was cut and the separate zones eluted with absolute alcohol. On evaporation of solvent a fourfold division was obtained ; a resinous impurity, and three waxy solids varying in melting-points—70°, 68°, 50·5°.

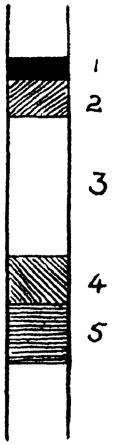

FIG. 3 (XIV[3])
Chromatogram from anthracene-sections showing differences in fluorescence

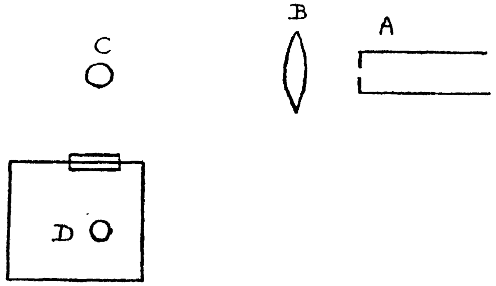

FIG. 4 (XIV[3])
The spectro-chromatogram apparatus of Almasy

The use of a quartz tube for fluorescence analysis is not essential ; tubes of soda glass are quite satisfactory ; if necessary, the column may first be extruded from the tube, and then examined in the ultra-violet.

(ii) **Formation of Coloured Derivatives.** This method consists in attaching to the material an easily removable chromophoric group, before, during, or after carrying out the analysis. Visual separation is thus effected through the picrates, ketones, or di-nitrobenzoates, and the colourless substance is re-generated after the process.

Reich attained a separation of glucose and fructose via their azobenzene-*p*-benzoyl esters. The sugars are first esterified by treating with azobenzene-

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[1] Devlin and Reilly (unpublished work).

p-benzoyl chloride in pure pyridine. The crude esters are partially purified by crystallization from organic solvents. The column is prepared from a slurry of silica especially prepared (in petroleum-benzene 3 : 1). This is poured into the tube and the usual procedure followed.[1]

In Reich's experiment he percolated a solution of 200 mg. fructose ester and 200 mg. of glucose ester in 40 ml. of chloroform, 80 ml. of benzene, and 80 ml. of petroleum. For the development of the chromatogram, 800–900 ml. of benzene-petroleum mixture (25 : 75) were filtered through the column ; the distribution of the chromatogram is illustrated in Fig. 5 (XIV³).

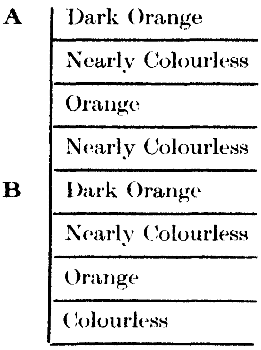

FIG. 5 (XIV³)
Chromatogram from mixture of azobenzene-*p*-benzoyl esters of glucose and fructose

Each layer was scraped out and eluted separately with a (2 : 8) mixture of methyl alcohol and chloroform. Layer A and Layer B yielded fructose and glucose esters which were identified by their specific rotary constants, and found to be practically pure. A second adsorption carried out on the individual fractions leads to the isolation of the pure substances. The individual sugars can be re-generated by saponification.

(iii) **Use of Colour Reactions for Rendering Chromatograms Visible.** If a dye is available whose adsorptive affinity is similar or proportional to that of the material under examination, then this third method of recognizing the zones can be applied. The dye can be incorporated in the solution which is to be chromatographed and its exact location on the column indicates the position of the required zone.

Brockmann and Busse when isolating Vitamin D from Blue Fin Tima Liver Oil used Indicator Red 33.[2] The concentrated oil from the unsaponifiable fraction was dissolved in petroleum ether and extracted sixteen times with 90 per cent methyl alcohol. The petroleum solution now contained 50·3 grams of substance, of which 28·2 grams were dissolved in 350 ml. of a 1 : 4 mixture of benzene and petroleum, to this 0·5 gram of Indicator Red was added. On chromatographing the solution on an aluminium hydroxide tube, and developing with pure solvent the tube read : reddish-brown—red—brown—bright yellow. The red zone was eluted and chromatographed from the same solvent : once again a red zone was visible, which was eluted and re-chromatographed. The red zone in the final chromatogram was eluted, the sterols and Indicator Red removed, and the residue was esterified

[1] Reich, *Biochem. J.*, 1939, *33*, 1000.

[2] *Z. physiol. Chim.*, 1937, *176*, 249.

with 3 : 5 di-nitrobenzoyl chloride. The crude ester was purified by dissolving in a mixture of acetone and methyl alcohol, and chromatographed on the same adsorbent : the lowest zone was eluted and the residue crystallized from acetone-methyl alcohol mixture.

Graff and Skau have separated higher fatty acids using as an indicator phenol red (phenolsulphonphthalein).[1] Magnesium oxide impregnated with phenol red was mixed with petroleum ether in the form of a slurry and poured rapidly into a tube 70 cm. in length and 12 mm. in diameter. The adsorbent was allowed to settle under a layer of solvent for several hours—a uniform column being thus obtained. The fatty acid mixtures were dissolved in petroleum ether and added to the column ; when the solution came in contact with the adsorbent a bright yellow band was formed which separated into zones on development.

The chromatogram was developed by allowing petroleum ether to percolate through the adsorbent continuously until clearly defined zones were obtained. The column was run dry, extruded from the tube, and cut into the sections indicated by the different colours. Each section was lixivated with hydrochloric acid and the fatty acids extracted with di-ethyl ether. By means of this procedure the authors were able to demonstrate a method of separating : (1) an unsaturated fatty acid from a saturated fatty acid of the same number of carbon atoms, and (2) two saturated fatty acids differing in length of chain by four carbon atoms.

A chemical test may be applied all along the column after it has been extruded from the tube : an example is a mixture of benzidine and naphthylamine in aluminium oxide ; if a brush dipped into a solution of lead peroxide in 30 per cent acetic acid is stroked along the length of the column, a streak showing blue at the top (benzidine) and green below (naphthylamine) is obtained. In some cases the brush method gives a streak which although colourless has ultra-violet fluorescence, which can be observed under the quartz mercury lamp.

(iv) **The Empirical Method.** When other methods fail, it is always possible to fractionate the column, and examine each eluate. The fractions may in turn be re-chromatographed on separate columns and again fractionated if necessary. In general, the separation is so sharp that a thorough examination of the first set of eluates will indicate the approximate position on the column of the substance under investigation.

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[1] *Ind. Eng. Chem. Anal.*, 1943, *15*, 340.

SECTION 3: SEPARATIONS

During the process of chromatography when the solution comes in contact with the first thin layer of adsorbent, all the solutes are deposited. Those of lower adsorption affinity are, however, displaced by solutes of greater affinity that immediately follow. Thus the weaker components leave the solid phase and return into solution, to be re-adsorbed by the next layer of adsorbent, where again they undergo displacement.

The concentration of the original solution slowly diminishes as it proceeds down the column: it can thence be seen that the solutes will be concentrated in bands in descending order of their adsorption affinities. If the chromatogram is now developed with pure solvent, the solutes are re-dissolved according to their individual adsorption coefficients: suppose the first band occupies only one thin layer of adsorbent -- now, the pure solvent re-dissolves this band and moves one layer forward, where it encounters a layer of adsorbent free of solute, adsorption begins anew, and pure solvent passes on: for a band consisting of many layers the mechanism is similar.

The concentration of any one solute in the developing medium increases from zero to a limiting value and then again falls to zero. The rate of development and of the movement of the zones is dependent on partition of the solute between the solvent and the adsorbent; by the use of different developing media, the picture can be altered at quite different speeds as well as to various extents.

If the solute has only a slight affinity for the adsorbent then it may easily be developed, as no difficulty will be experienced in re-dissolving it; if on the other hand the adsorption affinity is very strong, then the process of development is more difficult and bigger quantities of solvent must be used.

Wilson was one of the first to investigate the phenomenon of chromatography mathematically; he proposed a theory, which is reproduced here, slightly elaborated for simplicity.[1]

The Chromatography of a Solution containing One Solute. Consider a long column which contains M grams of adsorbent per cm. of its length; we wish to calculate the distribution of adsorbed material in the column after a volume v of a solution containing solute at an initial concentration c_0 has passed through it. Assume that equilibrium between adsorbed material and the solution in contact with it is always maintained and that the volume of the interstices between the particles of adsorbent per unit length of the column is negligible. Let the isotherm which represents the adsorption of the given solute on the adsorbent be:

$$q/m = f(c) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where q is the number of millimoles of solute adsorbed on m grams of adsorbent in equilibrium with a solution whose concentration is c moles per litre. Then under equilibrium conditions at any point in the column where the concentration of solute is c there will be adsorbed Q millimoles of solute per centimetre length of the column where:

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[1] *J. Amer. Chem. Soc.*, 1940, *62*, 1583.

$$Q = Mf(c) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let the distance from the top of the column to any lower point in the column be x, and consider the changes in Q and c which occur at x when an element of volume dv of solution, whose concentration at x is c, passes through a thin cross-sectional layer of the column of thickness dx, on which is adsorbed initially an amount Qdx of solute.

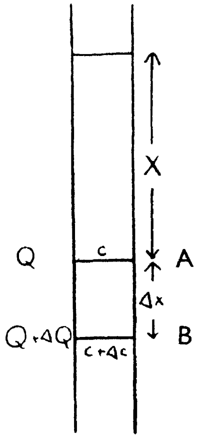

FIG. 6 (XIV³)
Chromatograph of a solution containing one solute

Consider Fig. 6 (XIV³). Amount being adsorbed at A $= Q\Delta x$. Amount being adsorbed at B $= (Q + \Delta Q)\Delta x$. Then the change in the amount being adsorbed is $\Delta Q\Delta x$. Now

$$Q = f(v, x)$$

$$\therefore \ dQ = (dQ/dv)dv + (dQ/dx)dx$$

At a definite distance x,

$$dQ = (dQ/dv)_x dv$$

Therefore $\qquad dQdx = (dQ/dv)_x dvdx$

Hence the number of millimoles of solute adsorbed on the layer x as

$$\Delta\, x \longrightarrow dx \longrightarrow 0$$

will change by an amount $(dQ/dv)_x dvdx$,

$$Lt \Delta Q\Delta x = dQdx, \ \Delta Q \longrightarrow 0, \ \Delta x \longrightarrow 0.$$

Again the concentration at A $= c$, and the concentration at B $= c + \Delta c$; thus the change in concentration is Δc

$$c = f(x, v)$$

$$\therefore \ dc = (dc/dx)dx + (dc/dv)dv$$

Considering a particular volume v of definite initial concentration then $dc = (dc/dx)_v dx$, that is the concentration of the solution passing through the layer (as $\Delta x \longrightarrow dx$) will change by $(dc/dx)_v dx$ $Lt \Delta c \longrightarrow 0 \Delta c \longrightarrow dc$. The number of millimoles of solute contained in the volume dv of solution will therefore change by an amount $(dc/dx)_v dxdv$. (These expressions will be positive or negative according as the adsorption increases or decreases on the layer.) Since the total amount of solute remains unchanged, we have

$$(dQ/dv)_x dvdx + (dc/dx)_v dvdx = 0 \quad . \quad . \quad . \quad (3)$$

Since $dvdx$ is definitely not equal to 0

then $\qquad (dQ/dv)_x + (dc/dx)_v = 0$

Substituting for Q from equation (2) we obtain as the differential equation for the chromatography of a single solute:

$$(d(Mf(c))/dv)_x + (dc/dx)_v = 0 \quad . \quad . \quad . \quad (4)$$

The general solution of this equation is:

$$c = \varphi(v - Mxf'(c)) \quad . \quad . \quad . \quad . \quad (5)$$

where φ is an arbitrary function and $f'(c)$ is equal to (df/dc). This is the all-important equation and can be applied either to the process of formation of the chromatogram or the process of development. Different boundary conditions will apply to the two cases.

Let the chromatogram be formed by pouring a volume v of a solution whose initial concentration is c_0 through the column. The appropriate boundary conditions are:

(*a*) when $v = 0$, $f(c) = 0$ for $x = 0$
i.e. no liquid, no chromatogram

(*b*) $v > 0$, $f(c) = f(c_0)$ at $x = 0$
with a definite volume of concentration c at the surface of the column $f(c) = f(c_0)$, and thereafter the concentration depends on x.

(*c*) $vc_0 = \int_0^\infty Qdx = \int_0^\infty Mf(c)dx$
This is a conservation condition—the total quantity of solute originally present vc must be equal to the quantity adsorbed, i.e. $\int_0^\infty Qdx$. . . . . (6)

It has been found that the first two boundary conditions are satisfied only by a discontinuous solution: $\varphi = \text{const.} = c$ up to a certain value of x, say x_0; $\varphi = 0$ beyond that value. Applications of conditions (2) and (3) lead to the solution:

Up to a certain value of x, $\varphi = \text{const.}$, i.e. $Q = Mf(c_0) = \text{const.}$ Since

$$vc_0 = \int_0^\infty Qdx = \int_0^\infty Mf(c)dx = \int_0^x Mf(c_0)dx + \int_{x_0}^\infty Mf(c)dx$$

where x_0 is the critical value of x. From $x_0 \longrightarrow \infty$, $c = 0$, if the concentration is zero then $Q = 0$, therefore $f(c)$ must $= 0$. The above then becomes:

$$vc_0 = \int_0^{x_0} Mf(c_0)dx = Mf(c_0)x_0$$

Therefore the critical value of $x_0 = vc_0/Mf(c_0)$.

Conclusions: (*a*) when x lies in the region 0 to $x_0 = vc_0/Mf(c_0)$ then $Q = Mf(c_0)$
(*b*) when x lies beyond this region: $Q = 0$. . . . . . (7)

The discontinuous nature of the solution (7) accounts in a satisfactory way for the sharpness of the bands observed in chromatographic experiments; the result is also in accordance with the experimental observation that the intensity of colour is approximately uniform throughout the band ($Q = Mf(c_0) = \text{const.}$).

Development. We may now consider the case in which a band already formed is developed by passage through the column of a volume V of some solvent not necessarily the same as the solvent used in forming the band. Let the adsorption isotherm for the solute in the developing solvent be

$$q/m = F(c) \qquad . \quad . \quad . \quad . \quad . \quad (8)$$

We assume that the band was formed in accordance with equations (7), i.e. that up to some point $x = x_0$, $Q = Q_0 = \text{const.}$; beyond x_0, $Q = 0$. We may also write:

$$Q_0 = Mf(c_0) = MF(c_0') \quad . \quad . \quad . \quad . \quad (9)$$

where c_0' is the concentration in the new solvent of volume V for equilibrium with Q_0. The boundary conditions to be applied are:

(i) When $V = 0$ (that is before adding the pure solvent for development purposes) original conditions hold. That is when x lies between x_0 and zero $Q = Q_0 = MF(c_0') = \text{const.}$

(ii) When the solvent just comes in contact with the surface $V > 0$ and $x = 0$ then since no solute has yet been re-dissolved $Q = MF(c) = 0$.

(iii) When all the solute has been re-dissolved, which amount will be equal to the original amount present, then:

$$vc_0 = \int_0^{\infty} Q_0 dx = \int_0^{x} MF(c)dx \qquad . \quad . \quad . \quad (10)$$

Consider Fig. 7 (XIV³). All the solute must be re-dissolved by developing solvent before it can again be re-adsorbed by the adsorbent. Therefore

$Q = 0$ when x lies between 0 and $Vc_0'/MF(c_0') = x_0$, and when it lies beyond $x_0 + Vc_0'/MF(c_0')$ because then all the solute has been re-adsorbed. $Q = Q_0 = MF(c_0')$ when x lies between x_0 and $x_0 + Vc_0'/MF(c_0')$. . . . (11)

The conclusion is thus reached that the band should remain sharp during the process of development and that its width should remain constant as it moves down the column.

The solutions 7 and 11 have been verified for the special case of the isotherm $f(c) = Kc$, where K is a constant, by an independent method in which the column was considered as being divided up into a large number of thin layers perpendicular to the tube. The process of formation or development of the chromatogram was treated as a succession of steps; in each step a small element of volume of solution was allowed to pass through the column layer by layer, coming into equilibrium with each layer in turn. The overall effect was obtained by summing the effects of the individual steps in the process; a limiting value was then found for the summation by letting the thickness of the layers and the magnitude of the elements of volume become infinitesimal. The method just outlined has the advantage of making clear the physical reason for the discontinuous nature of the bands: as an infinitesimal element of volume of solution passes over an infinitesimal element of length of column just beyond the leading edge of the band, it deposits an infinitesimal amount of solute. The concentration of solute in the element of volume decreases in this process,

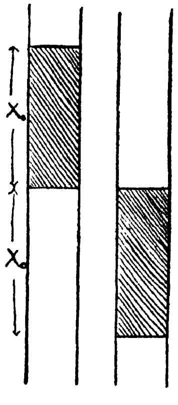

FIG. 7 (XIV³)

however, by a finite amount, so that the concentration of the solution becomes zero in a small number of infinitesimal steps, i.e. within an infinitesimal distance from the leading edge of the band.

In the development of equations 7 and 11 it has been assumed that the volume of the interstitial space between the particles of adsorbent is negligible, and that the volume v of solution or V of developing solvent is passed completely through the column before measurement of the width and position of the band is made. In actual practice the interstitial volume is not negligible, and the developing solvent is added as soon as all of the original solution has entered the column, and is added continuously until the development has been carried to a convenient stage. If these facts are taken into account the treatment of the problem is a little altered.

Let the volume of the interstitial space be α ml. per centimetre length of the column.

Total amount of solute vc_0 = amount adsorbed + amount in the interstitial spaces.

i.e. $$vc_0 = \int_0^{x_0} Q\,dx + \alpha c_0 x_0 = Mf(c_0)x_0 + \alpha c_0 x_0.$$

$$\therefore\ x_0 = vc_0/Mf(c_0) + \alpha c_0.$$

This then is the initial width of the band when a volume v has entered the column. The edges of the band are sharp as before and the adsorption Q per centimetre length of the band has the uniform value $\alpha c_0 + Mf(c_0)$ millimoles.

Consider the development of this band, assuming that the same solvent as was used in forming the band is added as soon as the solution has all entered the column. When a small volume ΔV of solvent enters the column the liquid within the column will be displaced a distance $\Delta V/\alpha$. A volume ΔV of solution whose concentration is c_0 will leave the lower edge of the band and will form an extension to the band of width $Vc_0/\{\alpha c_0 + Mf(c_0)\}$. Suppose the upper edge of the band has meantime migrated a distance Δx. Since the liquid between this point and the point $x = 0$ has not passed through any part of the band, the volume of solvent which has been used to dissolve the solute formerly adsorbed between $x = 0$ and $x = \Delta x$ is $\Delta V - \alpha\Delta x$. If the concentration of the solute in this volume of solvent has reached the value c_0 then :

$$(\Delta V - \alpha\Delta x)c_0 = Mf(c_0)\Delta x$$

whence $$\Delta x = \Delta V c_0/\alpha c_0 + Mf(c_0)$$

we conclude that the band should maintain the constant width

$$vc_0/\{\alpha c_0 + Mf(c_0)\}$$

and should migrate at a rate $c_0/\{\alpha c_0 + Mf(c_0)\}$ cm. per ml. of developing solvent added to the column, provided the same solvent is used in the developing of the band as was used in forming it. A similar analysis may be used to discuss the case in which a new solvent is used for development whose adsorption isotherm is $q = mF(c)$; as in the previous treatment (equation 9) let $f(c_0) = F(c_0')$, then it is shown readily that the width of the band will change to $vc_0/\{\alpha c_0' + Mf(c_0)\}$; after it has reached this value the width will remain constant and the band will migrate at a rate

$c_0'/\{\alpha c_0' + Mf(c_0)\}$ cm. per ml. of developing solvent added to the column. In practice the width of the bands varies widely with changes in the nature of the developing solvent.

Chromatography of Mixtures. The treatment of the formation and development of a chromatogram containing a mixture of solutes is very simple if the solutes are independently adsorbed, i.e. if the adsorption isotherm of each solute is a function of the concentration of that solute alone. In that case (the volume of the interstitial space being neglected for convenience) each of the solutes will form a uniform band of width $\frac{vc_i^0}{Mf_i(c_i^0)}$, where v is the initial volume of the solution, c_i^0 is the initial concentration of the ith solute, and $f_i(c_i)$ is the corresponding adsorption isotherm. These bands, each of which has its origin at $x = 0$, will overlap ; if the solutes are coloured the resulting chromatogram will appear as a series of contiguous colour zones, throughout each of which the colour is constant. On development with the original solvent each of the bands will move independently of the others at a rate equal to $\frac{c_i^0}{Mf(c_i^0)}$ cm. per c.c. of developing solvent drawn through the column. In general, the rates will be different and after sufficient development the bands will be completely separated, and will have, according to the present treatment, their original width and intensity.

Wilson, continuing, states that in many cases the adsorption of one solute is affected by all other solutes present, so that the adsorption isotherm of the ith solute in a solution containing n solutes, is a function of the concentration of all the solutes. Thus writing for the ith solute

$$q_i = mf_i(c_1, c_2, c_3, c_4, c_5, c_6 \ . \ . \ . \ c_n)$$

Wilson discusses the formation and development of such a mixed chromatogram.

The theory accounts for the qualitative features of chromatography in a satisfactory way, and provides a convenient basis from which a more precise theory may be developed. The effects of diffusion, which in this theory are assumed negligible, often cause trouble in practice. If the solute is not very strongly adsorbed the lower edge of the chromatogram is seldom sharp and more often than not indefinite ; again even in carefully packed columns the bands sometimes are concave rather than horizontal. This latter defect may in part be due to the fact that the velocity of the solvent is not uniform, as, often, the velocity near the centre is greater than at the walls.

A second and later theory has been developed by Martin and Synge, who considered the chromatogram to be closely analogous in its mode of operation to distillation and extraction fractionating columns.[1]

The behaviour of a column consisting of a number of ' theoretical plates ' within each of which perfect equilibrium between the two phases occurs, can be described with great simplicity. Peters [2] showed that the continuous or packed type of distillation column (in which equilibrium is not established at any point) could be divided up into a number of layers each of which was equivalent to one theoretical plate, and the height of such a layer was

[1] *Biochem. J.*, 1941, *35*, 1359.

[2] *Ind. Eng. Chem.*, 1922, *14*, 476.

called the H.E.T.P., or the 'height equivalent to one theoretical plate'. For the present purpose the H.E.T.P. is defined as the thickness of the layer such that the solution issuing from it is in equilibrium with the mean concentration of the solute in the non-mobile phase throughout the layer. It can be shown from diffusion arguments that the H.E.T.P. is a constant throughout a given column except when the ratio of the concentrations of the solution entering and leaving the plate differs greatly from unity. It may be taken as a constant for the chromatogram without serious error. The following then is the second theory proposed by Martin and Synge (for simplicity, the mathematics is again slightly elaborated).[1]

In order to be capable of manipulating the equations Martin and Synge assumed that the diffusion of solute from one plate to another was negligible, and that at equilibrium the distribution ratio of one solute between the two phases was independent both of the absolute value of its concentration and of the presence of other solutes. This theory applies to partition chromatography (p. 310) devised by the same authors. The extension of the theory to the usual adsorption chromatogram is obvious when the adsorption isotherm is a linear function of the concentration of solute in the liquid phase.

Consider a chromatogram of many plates:

Let A = the area of cross-section of the column

A_S = the area of cross-section of non-mobile phase

A_L = the area of cross-section of the mobile phase

A_I = the area of cross-section of the inert solid ($A_S + A_L + A_I = A$)

V = the volume of solvent used in development of the chromatogram

α = the partition coefficient, i.e.

$$= \frac{\text{grams solute per ml. of non-mobile phase}}{\text{grams solute per ml. of the mobile phase}} \text{ at equilibrium}$$

$V = h(A_L + \alpha A_S)$

h = H.E.T.P.

$$R = \frac{\text{movement of position of maximum concentration of solute}}{\text{simultaneous movement of surface of developing fluid in empty part of the tube above chromatograph column}}$$

r = serial number of the plate measured from the top of the column downwards

Q_r = total quantity of solute in plate r

Consider the case where unit mass of a single solute is put into the first plate, and is then followed by pure solvent. We can draw up a table showing the quantity of solute in each plate after successive infinitesimal volumes of mobile phase δv have passed. There is unit mass of solute on Plate (1). The volume δv distributes itself about V and takes away a fraction $\frac{\delta v}{V}$ of solute to be deposited on the next layer. The chromatogram now stands:

on Plate (1) there is $\left(1 - \frac{\delta v}{V}\right)$ of solute

on Plate (2) there is $\frac{\delta v}{V}$ of solute

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[1] *Loc. cit.*

When the second volume δv is added it distributes itself about V and brings down $\frac{\delta v}{V}$ of solute on plate (1) i.e. $\frac{\delta v}{V}\left(1 - \frac{\delta v}{V}\right)$ thus leaving $\left(1 - \frac{\delta v}{V}\right)\left(1 - \frac{\delta v}{V}\right)$ behind. On reaching plate (2) the volume δv carries away $\frac{\delta v}{V}$ of solute on that plate, and deposits $\frac{\delta v}{V}\left(1 - \frac{\delta v}{V}\right)$; thus the total quantity of solute on plate (2) is $\frac{\delta v}{V}\left(1 - \frac{\delta v}{V}\right) + \left(1 - \frac{\delta v}{V}\right)\frac{\delta v}{V}$ or $2\left(1 - \frac{\delta v}{V}\right)\frac{\delta v}{V}$. Finally $\left(\frac{\delta v}{V}\right)^2$ is deposited on plate (3). Thus the chromatogram:

$$\text{when volume } 2\delta v \text{ is passed} \begin{cases} \text{on Plate (1) there is } \left(1 - \frac{\delta v}{V}\right)^2 \\ \text{on Plate (2) there is } 2\left(1 - \frac{\delta v}{V}\right)\frac{\delta v}{V} \\ \text{on Plate (3) there is } \left(\frac{\delta v}{V}\right)^2 \end{cases}$$

Generalizing then we may say that the solvent brings down to Plate $(r + 1)$ from plate (r), $\frac{\delta v}{V}$ of solute on plate r and it carries away $\frac{\delta v}{V}$ of solute on plate $(r + 1)$ leaving $\left(1 - \frac{\delta v}{V}\right)$ of the solute on plate $(r + 1)$. After any one operation the amount of solute on plate $(r + 1)$ is

$$\frac{\delta v}{V}\text{A solute on } r \quad + \left(1 - \frac{\delta v}{V}\right)\text{A solute on } (r + 1)$$

from which data the following table may be drawn up:

TABLE I

Vol. of solvent passed ($x\delta v$)	Serial number of plate				
	$r = 1$	$r = 2$	$r = 3$	$r = 4$	$r = 5$
0	1	0	0	0	0
1	$\left(1 - \frac{\delta v}{V}\right)$	$\frac{\delta v}{V}$	0	0	0
2	$\left(1 - \frac{\delta v}{V}\right)^2$	$2\left(1 - \frac{\delta v}{V}\right)\frac{\delta v}{V}$	$\left(\frac{\delta v}{V}\right)^2$	0	0
3	$\left(1 - \frac{\delta v}{V}\right)^3$	$3\left(1 - \frac{\delta v}{V}\right)^2\frac{\delta v}{V}$	$3\left(1 - \frac{\delta v}{V}\right)\left(\frac{\delta v}{V}\right)^2$	$\left(\frac{\delta v}{V}\right)^3$	0
4	$\left(1 - \frac{\delta v}{V}\right)^4$	$4\left(1 - \frac{\delta v}{V}\right)^3\frac{\delta v}{V}$	$6\left(1 - \frac{\delta v}{V}\right)^2\left(\frac{\delta v}{V}\right)^2$	$4\left(1 - \frac{\delta v}{V}\right)\left(\frac{\delta v}{V}\right)^3$	$\left(\frac{\delta v}{V}\right)^4$

We see that the quantity in each plate is a term of the binomial expansion

$\left\{\left(1 - \frac{\delta v}{V}\right) + \frac{\delta v}{V}\right\}^n$ so that when n successive volumes of solvent δv have passed,

$$Q_{r+1} = \frac{n!\left(1 - \frac{\delta v}{V}\right)^{n-r}\left(\frac{\delta v}{V}\right)^r}{r!(n - r)!}$$

When n is large we may apply Poisson's approximation to the binomial

$$\left[{}^nC_xP^x(1 - P)^{n-x} = \frac{m^x}{x!}e^{-m}\right]$$

where $np = m$

thus $$Q_{r+1} = \frac{1}{r!}\left(\frac{n\delta v}{V}\right)^r e^{-\frac{n\delta v}{V}}$$

But $n\delta v$ is the volume of solvent that has been used to develop the chromatogram. Putting $n\delta v = v$

$$Q_{r+1} = \frac{1}{r!}\left(\frac{v}{V}\right)^r e^{-\frac{v}{V}}$$

which by Stirling's approximation becomes

$$Q_{r+1} = \frac{1}{\sqrt{2\pi r}}\left(\frac{v}{rV}\right)^r e^{\frac{nr}{V}} \quad . \quad . \quad . \quad . \quad (1)$$

when r is large (> 10)

Movement of the Band. Now Q_{r+1} is a max. and equals $\frac{1}{\sqrt{2\pi r}}$ when $\frac{v}{rV} = 1$ so that the position of max. concentration has moved a distance $\frac{hv}{V}$ directly proportional to the volume of liquid v which has flowed through. In terms of the movement of the surface of the liquid standing above the solid in the tube, the relative rate of movement R is given by the expression

$$R = \frac{vh/V}{v/A}, \text{ i.e. } \frac{\text{movement of band}}{\text{movement of surface}}$$

$$= \frac{Ah}{V}$$

$$= \frac{A}{A_L + \alpha A_S} = \frac{A_L + A_S + A_I}{A_L + \alpha A_S}$$

$$\alpha = \frac{A}{RA_S} - \frac{A_L}{A_S}$$

On plotting the concentration of solute on plate $(r + 1)$ against $\frac{v}{V}$ using equation (1), Martin and Synge obtained a curve which becomes the normal curve of error when r is infinite; continuing on these lines they are able to demonstrate separations ideally obtainable.

Factors influencing the H.E.T.P. The height equivalent to a theoretical plate depends upon the factors controlling diffusion and upon the rate of flow of the liquid. There is an optimum rate of flow in any given case, since diffusion from plate to plate becomes relatively more important the slower the flow of liquid and tends of course always to increase the H.E.T.P. Apart from this, the H.E.T.P. is proportional to the rate of flow of liquid and to the square of particle diameter. Thus the smallest H.E.T.P. should be obtainable by using very small particles and a high pressure difference across the length of the column. The H.E.T.P. depends also on the diffusibility of the solute in the solvent employed, and in the case of large molecules, such as proteins, this will result in serious decrease in efficiency as compared with the solutes of molecular weights of the order of hundreds.

Practical Limitations of the Theory. The separations obtainable in practice are less than the theory predicts for two principal reasons. First, the partition coefficient is seldom a constant, usually decreasing as the solution becomes stronger. This results in the front of the band becoming steeper, and the back flatter, and, more importantly, in the band becoming wider, since the concentrated part moves faster than the dilute part. This effect can sometimes be diminished by working with initially dilute solutions. Interaction between the two solutes often, however, leads to an increase in separation over the theoretical, the more strongly adsorbed solute ‘ eluting ’ the less strongly adsorbed, and thus tending to cause a sharp boundary between the two, reminiscent of the behaviour of ions in the moving boundary in transport number determinations. The other great source of loss of efficiency lies in lack of uniformity of flow through the column. This lack of uniformity often prevents good separations being realized, even though the solutes be separated in the column itself, as the cut cannot follow the required surface. In striving for conditions for uniformity of flow, the high pressure and small particle size desirable for smallest H.E.T.P. have to be abandoned.

In criticizing Wilson's theory, Martin and Synge emphasize the fact that he neglects all diffusion and lack of equilibrium, i.e. in their nomenclature assumes h as zero, and again that he attempts a general solution for the case that the partition coefficient (adsorption isotherm) is not constant (linear). The discontinuous solution at which Wilson arrives is in fact true only in the case in which the partition coefficient is a constant, hence they conclude that the greater part of his paper is invalidated. His equation for the rate of movement of the band reduces to the same as their equation (2) when the partition coefficient is a constant ; but as it stands it implies the absurd result that a square-fronted band is propagated unchanged while a band of any other shape changes shape during development.

Experimentally the same authors proved the relationship between the movement of the band and partition coefficient as follows : A column was started using a solution of 2 mg. each of acetyl-*l*-proline hydrate and acetyl-*dl*-phenylalanine. The column had 1 cm. diameter and length 20 cm., it was developed with chloroform and 1 per cent of (v/v) n-butyl alcohol until the bands were well separated. The movement of the centre of each band for a given movement of the liquid surface above the column was then measured. The column contained 5 grams of dry silica, 3·5 ml. of water and 10 ml. of chloroform phase. Hence, assuming the density of silica to be 2·3 grams/ml., $A_I = 0{\cdot}11$ cm.², $A_S = 0{\cdot}175$ cm.² and $A_L = 0{\cdot}5$ cm.² From equation (2) the value of the partition coefficient may be calculated :

$$\alpha = \frac{A}{RA_S} - \frac{A_L}{A_S} = \frac{4{\cdot}5}{R} - 2{\cdot}8$$

In Table II the values of α found thus, and by direct titration of the two phases after shaking together in a separating-funnel are given for the two acetamino-acids. The values for α as determined by the two methods are in good agreement.

TABLE II

Acetamino-acid	R	α (determined from band rate)	α (determined directly)	c (mg. of solute per ml. aqueous phase in direct determination)
Acetylproline . . .	0·37	9·4	9·5	10
Acetylphenylalanine .	1·07	1·4	1·3	2

TABLE III

RATE OF BENZENE FLOW THROUGH CALCIUM HYDROXIDE COLUMNS

(17 mm. in diameter and 150 ± 5 mm. long)

The data given indicate flow in mm. column length/min. Time was measured from the instant the solvent was poured on the column.

Column No.	1	5	10	15	20	25	30	35	40
1	32·0	14·5	9·0	7·1	6·4	6·3	6·3	—	—
2	43·0	15·5	9·8	7·1	7·0	7·0	7·0	—	—
3	36·0	13·5	7·8	—	7·6	7·5	7·5	7·5	—
4	42·0	15·3	—	—	7·6	7·7	7·7	7·7	7·7
5	43·0	13·8	8·8	—	8·4	8·2	8·2	8·2	8·2
6	42·0	16·0	13·0	—	—	8·1	8·1	8·1	8·1

The solvent reached the bottom of the column in about 12 minutes.

Standardization of Chromatography. Since these two foregoing theories had been developed, it was now possible to formulate a method of standardizing chromatography ; in this respect Le Rosen has recently proposed the following method.[1] The investigations recorded were undertaken primarily with the purpose of ascertaining how far it is possible to determine the relative position of carotenoids on the adsorbent column by separate measurements of the rate of movement for each pigment. The flow of the developing solvent through the adsorbent was first investigated. The velocity of flow was found to vary directly with the pressure difference between the ends of the column, inversely with the length of the column and to be essentially independent of the diameter of the tube. The change of rate of flow with time was of importance, and Table III illustrates the behaviour of calcium hydroxide columns. It is evident that the flow becomes constant after an initial decrease, a uniform rate being obtained soon after the solvent has reached the bottom of the column.

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[1] *J. Amer. Chem. Soc.*, 1942, *64*, 1905.

To simplify the discussion three terms were introduced :

S = length of adsorbent column containing one unit volume of solvent/length of tube required to contain the same volume of solvent

V_c = rate of flow of developing solvent through the column when a state of constant flow has been reached (mm./min.)

R = rate of movement of adsorbate zone (mm./min.)/rate of flow of developing solvent (V_c)

The ratio S is of importance in characterizing the packing of the column, and, moreover, it gives the percentage of the tube volume occupied by the adsorbent (per cent volume adsorbent = 100(S − 1)/S). There is a variation in the degree of packing throughout the column ; S was found to vary on the average from 1·97 for the top third to 1·79 for the bottom third of the calcium hydroxide columns used. No consistent relation was observed between S and V_c, probably due to the greater importance of local variations in the column packing. The rate of solvent flow, V_c, varies from column to column packed with the same adsorbent under similar conditions, but the variation is within reasonable limits ; for example, in 14 of 15 cases considered, V_c was between 6·3 and 8·2, while in one instance it was much higher than 10·3.

The ' strength ' or adsorption affinity of a material may be best determined by measuring the adsorption isotherm ; this, however, is not always practicable, but the same end can be attained by measuring R, the relative rate of movement of an adsorbate zone with respect to the developing solvent. Table IV gives the values of R for certain carotenoids, and Table V shows the agreement of the relative positions of carotenoid zones, calculated from R, and positions observed when a mixture was separated chromatographically.

From measurements of R, certain inversions were predicted by Le Rosen of the relative positions of pairs of carotenoids on different adsorbents. The first example was the case of kryptoxanthin-lycopene ; kryptoxanthin is adsorbed above lycopene on calcium carbonate or alumina but below on calcium hydroxide. This phenomenon had already been noticed by Duschinsky and Lederer.[1]

In concluding, Le Rosen [2] states that measurements of V_c of adsorbents leads to the acquirement of better materials before use. For ordinary laboratory work a range of from about 5 to 15 mm./min. is desirable ; this seems to be associated with an average particle size of 5 to 15 microns. If the adsorption affinity of a material shows much variation, as in the case of alumina, measurements of R for the substances to be separated should allow for standardization. The most suitable value for R seems to be between 0·2 and 0·3.

Determination of V_c. The tubes were filled with the adsorbent while the suction was applied (about 25 mm. vacuum) and the adsorbent slowly poured into the tube, the sides of which were then vigorously tapped in order to allow the adsorbent to settle. The top of the column was pressed down firmly with a stamper, and the adsorbent was removed from the walls of the column. Three successive 5-ml. portions of the solvent were then pipetted on to the top of the column. Just as each portion disappeared into the adsorbent the next one was introduced. At the same time, the position of the bottom edge of the solvent was noted. In this manner it was possible to determine the number of mm. column length equivalent to 1 ml. of solution. Next a burette was attached to the top of the adsorption-tube by a stopper provided with an outlet which could be closed when the air space above the column was filled with solvent. The burette stop-cock was then opened, the tube filled with solvent, and the outlet closed. It was then possible to determine the velocity of the solvent in the column from the flow in ml. per min. shown by the burette.

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[1] *Bull. Soc. Chim. Biol.*, 1935, *17*, 1534.

[2] *Loc. cit.*

TABLE IV

RATES OF MOVEMENT OF CHROMATOGRAPHIC ZONES RELATIVE TO THAT OF THE DEVELOPING SOLVENT, ON CALCIUM HYDROXIDE AND DEVELOPED WITH BENZENE

Measurements apply to the bottom edge of zone

Substance	R	Substance	R
Capsanthin	0·007	Lycopene	0·125
Celaxanthin	0·015	Kryptoxanthin	0·340
β-Carotenone	0·030	Physalein	0·590
Zeaxanthin	0·040	γ-Carotene	0·790
Lutein	0·070	Prolycopene	0·885
Hydroxy-γ-carotene	0·070	β-Carotene	1·000

TABLE V

CALCULATED AND OBSERVED RELATIVE POSITIONS OF THE COMPONENTS OF A MIXTURE SEPARATED ON CALCIUM HYDROXIDE, DEVELOPED WITH BENZENE

Zones were identified spectroscopically

Substance	Calculated		Observed position mm. from the top relative to lycopene	
	R	R/R lycopene	I	II
Capsanthin	0·007	0·056	0·04	0·04
Celaxanthin	0·015	0·120	0·13	0·11
β-Carotenone	0·030	0·240	0·24	0·19
Zeaxanthin	0·040	0·320	0·35	0·30
Lutein.	0·070	0·560 } not	0·62	0·55
Hydroxy-γ-carotene . .	0·070	0·560 } separated	0·62	0·55
Lycopene	0·125	1·000	1·00	1·00

Determination of R. The procedure was the same as described above except that the initial portion of solvent (ligroin or ligroin-benzene) contained the carotenoid pigment, while all succeeding portions were pure benzene. The solution was poured on the column in a solution containing ligroin, from which it is more strongly absorbed than benzene, in order to obtain a concentrated zone. The ligroin is immediately washed through the column by the benzene and, consequently, does not interfere with the determination. The burette reading and carotenoid position on the column were recorded at 10-minute intervals by a stop-watch. The values recorded in Table IV were observed when V_c was reached.

SECTION 4: PARTITION CHROMATOGRAPHY

A new chromatographical technique has been evolved by Martin and Synge,[1] which they termed partition chromatography. The adsorbent used in this procedure was liquid (water suspended in silica gel), and separation depended on differences in the partition between the two liquid phases, and not, as in all previously described chromatograms, on differences in adsorption between liquid and solid phases. As has already been discussed, when substances to be separated are coloured the procedure is very much simplified: if, however, colourless substances are used an indicator must be employed to render the zones 'visible'. Martin and Synge devised and used this form of chromatography for the separation and estimation of amino-acids formed by the hydrolysis of proteins, for which application they found methyl orange to be the most suitable indicator.

In applying this form of analysis to the micro-determination of mono-amino acids [2] in proteins they adopted the following procedure: commercial water glass (140° Tw.) is diluted to 3 volumes with distilled water containing a little methyl orange. 10 N hydrochloric acid solution is added in a thin stream with vigorous stirring, addition being interrupted at intervals and stirring continued to get efficient mixing. The solution changes first slowly and then rapidly to a thick viscous mass and all but the smallest lumps are broken up by the stirring. When the mixture is permanently acid to thymol blue, addition of acid is stopped and the mixture is kept 3 hours. It is then filtered on a buchner funnel and washed with distilled water (approx. 21/250 grams dry gel) without allowing the precipitate to crack. The gel is then suspended in N/5 hydrochloric acid solution and is aged 2 days at room temperature. It is again filtered and washed in the same way with distilled water (approx 51/250 grams dry gel) until the washings are free from methyl orange. Finally, the gel is crumbled and dried at 110° in an air oven. This dry gel can be stored in a closed vessel for long periods without deterioration.

The gel was prepared for the chromatogram by adding 50 per cent w/w of a saturated solution of methyl orange in water. The solution is added to the gel at once and thoroughly mixed in. A dry pink powder results, which barely adheres to the walls of the vessel in which it is mixed. An amount of this material containing 5 grams of silica is then suspended with stirring in about 35 ml. of chloroform saturated with water and containing 1 per cent v/v of *n*-butyl alcohol. At this point the colour of the gel changes from pink to yellow. The suspension is poured on the chromatogram tube (int. diam. 1 cm., length 30 cm.) furnished at its bottom with a double layer of filter-paper mounted on a perforated plate.

The gel packs down as the chloroform flows out at the bottom of the tube; being lighter than the chloroform in which it floats. When it has packed down to its final position, the top surface appears to be dry, and if evaporation is prevented, no further chloroform leaves the column, capillary forces preventing the entry of air. The gel does not float up again when fresh chloroform is carefully added at the top of the column. The solvent emerging at the bottom of the column is almost free from indicator, the methyl orange being firmly held in the aqueous phase.

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[1] *Biochem. J.*, 1941, *35*, 1358.

[2] *Ibid.*, 1941, *35*, 1364.

The substances for analysis are dissolved in a little chloroform-*n*-butyl alcohol and this solution is carefully added to the top of the column by allowing it to run from a pipette down the side of the chromatogram tube. When this addition and any washings have drained into the gel, the chromatogram is developed by adding fresh solvent at the top of the column.

The position of the acids is revealed by the indicator, which turns from yellow through orange to pink. As development proceeds the single pink band at the top of the column resolves into constituent bands which move down the column at characteristic rates.

About 100 grams of protein are hydrolysed by refluxing for 24 hours in 6 N hydrochloric acid solution, and the bulk of the acid is removed by repeated evaporation with water *in vacuo*. The material thus obtained is taken up in water and made alkaline to thymolphthalein by addition of 6 N sodium hydroxide solution and this is then concentrated *in vacuo* to a thin syrup. This is acetylated by the addition of 10 ml. of 2 N sodium hydroxide solution and 1 ml. of acetic anhydride in five equal portions in the course of 15 minutes. Between each addition the reaction vessel is thoroughly shaken and cooled with ice water. After this the mixture is allowed to remain alkaline to thymolphthalein for 10 minutes; 1 ml. of 10 N sulphuric acid is then added and the solution is concentrated *in vacuo* below 40° to about 5 ml. It is then acidified to thymol blue by further addition of 10 N sulphuric acid. The solution is transferred to a separating funnel at a volume of 10 ml. with water, and is extracted with five successive batches of 50 ml. of chloroform. The chloroform extracts are filtered through paper into a distilling-flask and are concentrated first at atmospheric pressure and finally *in vacuo* leaving a residue of amino acids which is made up in alcohol to 10 ml.

Three ml. of the alcoholic solution (corresponding to about 30 mg. of protein) are evaporated to dryness *in vacuo* in a small Erlenmeyer flask, and stored overnight over concentrated sulphuric acid and soda lime in a desiccator, to effect the removal of free acetic acid. The material in the flask is then transferred quantitatively to the chromatogram column in a minimum of chloroform-*n*-butyl alcohol, and the chromatogram is developed as described above with chloroform saturated with water and containing 1 per cent *n*-butyl alcohol. As each of the three bands passes out of the bottom of the tube, the chloroform receiver is changed. The solution collected is evaporated *in vacuo*, and the residue is taken up in a little water and titrated with 0·01 N. barium hydroxide solution using phenolphthalein as indicator. Care is taken to exclude carbon dioxide during the titration.

Later investigation by the same authors [1] leads to a discussion concerning the possibility of adsorption by the silica. Such an occurrence would seriously interfere with the analysis, irregular bands resulting, as well as 'tailing' of the solutes undergoing examination. Thorough acidification during the precipitation and ageing is also of importance in the preparation of the gel, as the retention of sodium ions is responsible for low recovery. The use of different solvent systems is discussed, interesting conclusions being drawn, which lead to a micro-method for the determination of mono-amino acids.

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[1] *Biochem. J.*, 1943, *37*, 79.

The choice of indicator for use in partition chromatography is a very important matter. Most of the indicators of suitable range are extracted readily from the aqueous phase by the developing solvent. The column thus becomes colourless and further visual separation of solutes is impossible. An indicator then must be used which will be soluble in the aqueous phase, and yet will not be easily 'leached' by the developing solvent. Methyl orange, the original indicator, is not free from this defect. Solvents of higher alcohol concentrations readily extract it from the aqueous phase.

Gordon, Martin, and Synge [1] have examined nine representatives of the anthocyanins as indicators and have recorded their observations. Liddell and Rydon [2] have found that the ammonium salt of the dye formed by coupling diazotized amino R-acid with N-phenyl-α-naphthylamine is an excellent indicator on 1 to 3 per cent *n*-butyl-alcohol-chloroform columns, and is not 'leached' when the *n*-butyl alcohol concentration is raised to 17 per cent.

Another variation of this type of chromatography has been introduced: Consden, Gordon, and Martin [3] have analysed proteins qualitatively using paper as an adsorbent. Using only 200 mg. of wool they were able by their new method to demonstrate the presence of all the amino acids which have been shown to be there by other methods. The cellulose (filter-paper) plays the rôle of the inert support, and separation depends on differences in partition coefficient between the mobile phase and water-saturated cellulose.

The most satisfactory solvents are those which are partially miscible with water. Within a homologous series of solvents the corresponding rates of movement of the amino acids change in the same direction as the water solubility of the solvent: solvents completely miscible with water can be employed provided that the water content is not too high. In this case, presumably, the cellulose, by a 'salting out' effect, allows the system to function as a partition chromatogram. However, the amino-acid bands obtained are much broader than is the case with imiscible solvents. This is no doubt due to a variation in the composition of the phases caused by the presence of the amino acids. This effect has been noticed in the *n*-butyl-alcohol-water system by England and Cohn [4] and is the limiting factor in the amount of amino acid that can be employed in a given chromatogram. It is reasonable to suppose that the phases will be more easily disturbed by employing a miscible rather than an imiscible solvent. The main effect of temperature on the rates of movement of the amino acids is also explicable in terms of the change in composition of the phases. Thus, in the phenol-water system, increase of temperature increases the miscibility and the rate

[1] *Biochem. J.*, 1944, *38*, 65.
[2] *Ibid.*, 1944, *38*, 68.
[3] *Ibid.*, 1944, *38*, 224.
[4] *J. Amer. Chem. Soc.*, 1935, *57*, 634.

of movement of the bands. In the collidine-water system the reverse is true. Further, the greater the difference between the working temperature, and the critical solution temperature, the less sensitive will the rates be to change of temperature. However, though the absolute partition coefficients may be greatly changed, the ratios of the partition coefficients of the respective acids are almost unaltered. There is an obvious advantage in working with unsubstituted amino acids in that any substituent group, even though small, renders the physical properties of the derivatives more similar and hence increases the difficulties for separation. Martin and Synge [1] and Gordon, Martin, and Synge [2] failed to separate the slower-moving acids when acetylated, whereas all the acids are separable by the present technique. Moreover, selective losses associated with acetylation and extraction are obviated.

A considerable number of solvents has been tried. The relative positions of the amino acids in the developed chromatogram depend on the solvent used. Hence by development first in one direction with one solvent followed by development in a direction at right angles with another solvent, amino acids (e.g. a drop of protein hydrolysate) placed near the corner of a sheet of paper become distributed in a pattern across the sheet to give a two-dimensional chromatogram characteristic of the pair of solvents used. Advantage is taken of the colour reaction with ninhydrin to reveal the positions of the amino acids.

Relation of Partition Coefficient to the Rate of Movement of the Bands. The relation of partition coefficient to the rate of movement of the band may be calculated from the method of Martin and Synge [3] where

A = cross-sectional area of paper water solvent,

A_L = cross-sectional area of solvent phase,
A_S = cross-sectional area of water phase,
α = partition coefficient,

$$= \frac{\text{concentration in water phase}}{\text{concentration in solvent phase}}$$

$$R = \frac{A}{A_L + \alpha A_S}$$

However, R is not conveniently measurable in paper chromatograms, so a new symbol R_F is introduced. This symbol R_F is equivalent to the symbol R used by Le Rosen.

$$R_F = \frac{\text{movement of band}}{\text{movement of advancing front of liquid}}$$

$$= \frac{RA_L}{A} = \frac{A_L}{A_L + \alpha A_S}$$

$$\text{or } \alpha = \frac{A_L}{R_F A_S} - \frac{A_L}{A_S} = \frac{A_L}{A_S}\left(\frac{1}{R_F} - 1\right)$$

A_L/A_S is equal to the ratio of the volumes of solvent and water phase in the chromatogram. Assuming a given water content of the paper, A_L/A_S may be deduced from the ratio of the weight of dry paper to that of the developed chromatogram.

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[1] *Biochem. J.*, 1941, *35*, 1358.

[2] *Ibid.*, 1943, *37*, 79.

[3] *Loc. cit.*

The water content of the paper is apt to vary from experiment to experiment and is difficult to measure in the presence of *n*-butyl alcohol or any other solvent. Table VI shows the partition coefficient calculated from the R_F and A_L/A_S values for four separate runs under slightly different conditions. The water content has been so chosen that the partition coefficient for glycine is equal to that given by England and Cohn.[1] The last column gives the direct measurements of England and Cohn.

TABLE VI

PARTITION COEFFICIENT CALCULATED FROM R_F VALUES

No. of run	1	2	3	4	Direct measurements England and Cohn (1935)
Per cent water in paper	28·7	18·0	22·6	17·7	
A_L/A_S	3·25	4·56	3·70	2·93	
PARTITION COEFFICIENTS					
Glycine	70·4	70·4	70·4	70·4	70·4
Alanine	35·9	39·9	43·7	36·6	42·3
Valine	12·2	14·1	14·8	12·5	13·8
Norvaline	8·7	10·8	10·5	9·2	9·5
Leucine	4·5	5·4	5·6	6·0	5·5
Norleucine	3·5	4·2	4·4	4·6	3·2

Experimental. The essentials of the apparatus consist of a filter paper strip, the upper end of which is immersed in a trough containing the water-saturated solvent. The strip hangs in an airtight chamber in which is maintained an atmosphere saturated with water and solvent. The trough is provided with a bar over which the paper passes to prevent

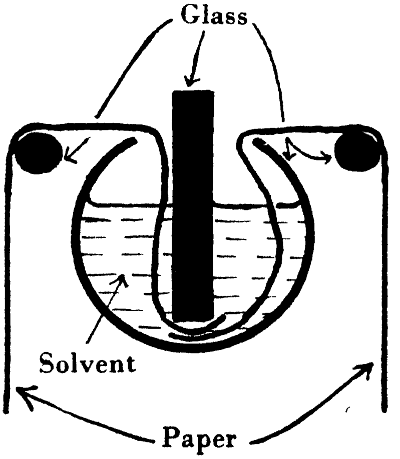

FIG. 8 (XIV³)
Cross-section of small trough

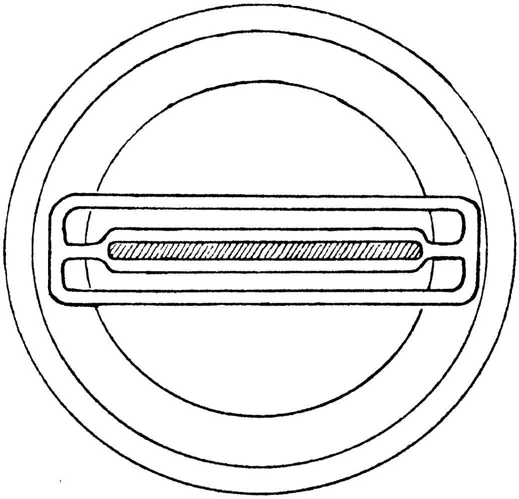

FIG. 9 (XIV³)
Plan of small trough in pipe

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[1] *J. Amer. Chem. Soc.*, 1935, *57*, 63.

capillary siphoning between the outside of the trough and the paper. The apparatus is shown in Figs 8, 9, and 10 (XIV^3).

Airtight Chamber. For one-dimensional experiments stoneware drain-pipes (6 or 9 in. in diam. and 2 ft. and 2 ft. 6 in. long respectively) have been found convenient. The pipe stands in a close-fitting tray hammered from a sheet of lead. The top of the pipe is ground flat and covered by a sheet of glass. The glaze on these pipes is imperfect and a pipe should be reserved for each solvent and atmosphere. For two-dimensional experiments the chamber consists of a glass-sided lead box, 30 × 30 × 5 in., made airtight with a well-fitting lead lid. A movable lead tray rests on the floor of the box. A completely airtight tinplate box, using the tray as a water seal, was used when an atmosphere of coal gas was required.

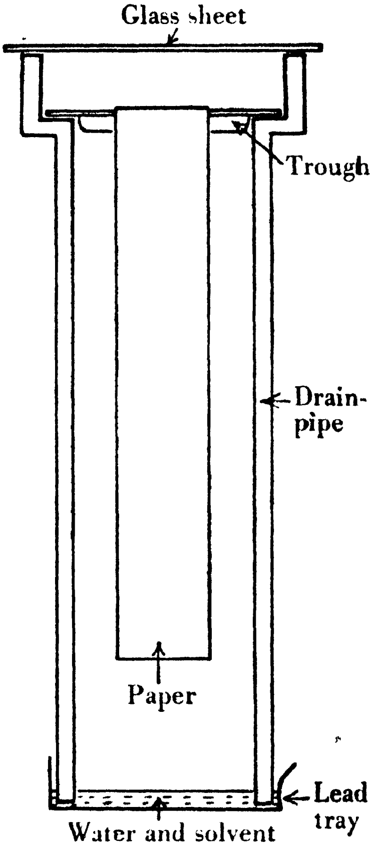

FIG. 10 (XIV^3)
Elevation of small trough in pipe

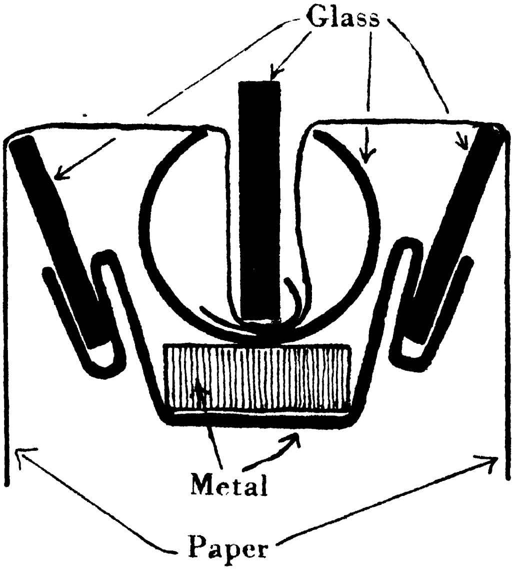

FIG. 11 (XIV^3)
Cross-section of large trough

Troughs. The troughs used in one-dimensional experiments are constructed from 0·4 in. bore glass tubing, opened along its length by grinding. For two-dimensional work, the larger troughs required would be too fragile if of the same pattern. Therefore an iron frame supports the trough (of 0·5-in. bore thick-walled tubing) and carries strips of sheet glass which replace the bars. The cross-section is shown in Fig. 11 (XIV^3).

Paper. Whatman No. 1 filter-paper has been used almost exclusively. Whatman No. 42, while giving satisfactory separations of amino acids, was too dense to permit a convenient rate of flow of solvent. In an attempt to separate larger quantities of amino acids, thicker papers have been tried. Of these, Whatman 'Accelerator' paper ($\frac{1}{26}$ in. thick) gave satisfactory separations but was too fragile to withstand normal handling. With most solvents the advancing front of liquid is coloured yellowish-brown by material extracted from the paper. This contaminant can be partially removed by soxhlet extraction with ethanol. Chromatographic washing is more effective.

Procedure. To run a one-dimensional chromatogram a strip of paper, 1·5 cm. or more in width and 20·56 cm. in length, is used. A pencil line is drawn across the strip about 5 cm. from one end. The solution, 2–4 ml. containing 5–15 mg. of each amino acid to be analysed, is applied along the centre portion of this line from the tip of a capillary tube. The end of the paper is fixed in the trough with a microscope slide. The trough and the paper are now transferred to the chamber, which has been previously prepared by covering the bottom of the tray with a two-phase mixture of water and solvent to provide an atmosphere saturated with both components. The trough is filled with water-saturated solvent and the lid put on the chamber. When the solvent has run a convenient distance (15–25 cm. in 6 hours; 30–50 cm. in 24 hours depending on solvent and temperature), the paper is removed and the position of the solvent front is marked. The strip is dried, either in an oven at 110° or by hanging in a drying-cupboard through which hot air is sucked by a fan exhausting to the outside. After drying, the paper is sprayed with a solution of ninhydrin (0·1 per cent in *n*-butyl alcohol) and again dried. Finally, the paper is heated at 80° for 5 minutes. The bands are outlined in pencil, as fading of the colour takes place after a few days. When it is desired to run a number of chromatograms simultaneously, the individual solutions may conveniently be placed side by side on a wide strip.

For two-dimensional analyses, a standard sheet 18 × 22½ in. is used. The solution to be analysed (6–12 ml., representing 200–400 mg. of protein) is placed near the corner, 6 cm. from either edge. The paper is held with one edge slightly overlapping the opening of the trough and pressed into it with a strip of sheet glass somewhat longer than the paper. After transfer to the chamber, prepared as above, the chromatogram is allowed to develop for 24–72 hours. The paper is then removed and dried in the drying-cupboard, turned through a right angle, and returned to the trough. The next stage of development, again for 24–48 hours, now proceeds, the chamber, tray and trough having been prepared for the second solvent during the drying of the sheets. Subsequent treatment is the same as for the strips. Throughout the manipulations, care must be taken not to touch the paper with the hand, as finger-marks will show after heating with ninhydrin. Strips are handled with forceps, and sheets with special wide clips.

In applying this type of chromatography to the analysis of proteins, a table of actual R_F values for amino acids was calculated, the positions of the different acids on the paper could then be predicted, hence unknowns could be identified.[1]

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[1] *Biochem. J.*, 1944, *38*, 65.

SECTION 5: TECHNIQUE

Apparatus. From time to time many and various forms of apparatus have been designed and used. To facilitate extrusion of the column without breaking, it is essential that the tubes should be uniform or else taper slightly towards the lower end. In general the size varies from 1 to 6 cm. in diameter and from 20 to 50 cm. in length. Some types of tubes are illustrated in Fig. 1 (XIV^3). In this example the tube is of uniform bore throughout, at the lower end a removable silver or platinum gauze is fitted. When the column is being prepared this gauze is covered with a pad of cotton-wool and the column is filled in the ordinary way. When the chromatograms are formed the column can easily be extruded by removing the gauze and cotton wool, and by pressing the adsorbent gently with a wooden or glass pestle. Another form illustrated in Fig. 12 (XIV^3) is described by Zeichmeister and Cholnoky ; [1] the tube is connected by a ground-glass joint to a short thistle funnel which fits into a filter flask. The tube may have a small constriction just above this joint, the column is supported on a perforated porcelain plate covered with a pad of cotton-wool ; a circle of wool 0·5 cm. thick and with a diameter of 2 cm. greater than the plate is wrapped over this so that the edges of the wool come below the plate when it is placed in the tube. In other tubes the perforated plate is mounted on the top of a thistle funnel, the pad of wool rests on this, and the two parts of the apparatus are joined by wire spirals ; in this case the parts must be connected before filling.

In the author's laboratory [2] tubes similar to Fig. 13 (XIV^3) have been used with excellent results. These are prepared by drawing out one end and mounting in a Buchner flask. A piece of cotton-wool is inserted in the lower end and the column filled with adsorbent in the usual way. The bands are quite easily and efficiently separated by scraping out with a special shaped glass rod (Fig. 14 (XIV^3)). Sintered glass discs have also been used to support columns, and glass wool used instead of cotton-wool. At the top of the tube there is a tap funnel for introducing the solution.

Crowell and Konig have described a special apparatus for chromatographical use.[3] A tube has been designed which permits one to follow the development of colourless chromatograms by brushing or spotting reagents on the surface of the adsorbent, with no loss of time or material, and also to test inorganic chromatograms with traces of reagents, while the bulk of the material remains in the tube in its original state.

The chief feature of the device is a section cut from a small portion of

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[1] Zeichmeister and Cholnoky, *Principles and Practice of Chromatography.*

[2] University College Cork.

[3] *Ind. Eng. Chem. Anal.*, 1944, *16*, 347.

the circumference of the tube along its entire length, forming a tight-fitting lid in the corresponding lengthwise opening. The first tubes were of glass but later ones were made of plastic (lucite). The latter are limited in their use to chromatograms in which only solvents are used which do not attack the plastic. The tubes used by Crowell and Konig are 240 mm. long with an inside diameter of 15 mm. They were machined from a 24-mm. round lucite rod, leaving a wall of thickness 4·5 mm. Two symetrical cuts converging at an angle of 90° were made along the entire length of the tube to produce an opening of 5 mm. wide on the inside and 13 mm. wide on the outside circumference. From a square-shaped lucite rod a corresponding circular segment was machined fitting smoothly into this opening, and after it was set in the tube the inside was machined perfectly smooth. A short section of the lower end of this two-piece tube was machined so as to reduce its diameter somewhat and produce a slight taper, and an adapter with suction tube made from lucite was fitted into it in such a way that it could not slip entirely up the taper. A clearance of about 15 mm. between the end of the tube and the base of the adapter served as a receptacle for the cotton. Near the top of the tube a groove was cut around its circumference and a steel position tension spring was fitted into it. This made possible an exact replacement of the lid after its removal. Metal bands with screw and nut hold the tube tightly together. The adapter is supplied with cotton,

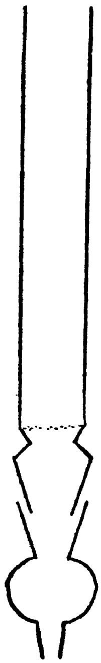

FIG. 12 (XIV[3])
Modified chromatograph tube

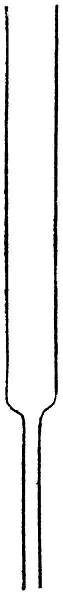

FIG. 13 (XIV[3])
Simple chromatograph tube

FIG. 14 (XIV[3])
L-shaped glass rod for separation of sections of the chromatogram

the tube is assembled and fitted into the adapter, the whole apparatus is inserted in a suction flask by means of a rubber stopper, the tube is filled in the ordinary way, and the chromatogram is started. Whenever desired the apparatus is taken from the flask, the adapter is carefully removed, the metal bands are taken off, and the lid is opened to make the necessary tests. If these indicate incomplete development, the lid is reset and the apparatus reassembled for further development.

Adsorbents. In general, the adsorbent must be capable of being dried by heating and be free from soluble impurities : these requirements rule out many organic compounds. Lactose and sucrose have been used. Inorganic substances must be neither strongly acidic nor strongly alkaline ; such substances might react chemically with the substances adsorbed, or might tend to hold them so firmly that separation into zones could not be carried out. Uniformity in adsorptive power of different parts of the same adsorbent is necessary, so that it is desirable that all the particles should be of a uniform size. The same chemical compound from different sources frequently varies in adsorptive power : advantage may be taken of this to obtain adsorbents of varying ‘ power ’, by using mixtures of such substances in different proportions. In general, moisture is harmful ; to take an extreme case, that of lime, it causes swelling which makes percolation and extrusion from the tube difficult. The most commonly used adsorbent is alumina, anhydrous or hydrated. Alumina may be activated by washing with tap-water and then strongly heating : the activation seems to be due to a small amount of lime taken up from the water ; Table VII shows the variation in activity under some conditions of preparation. The figures in the last column refer to the movement of a band of 1 mg. of α-carotene, initially in 50 ml. of light petroleum when washed on a standard column with a further 125 ml. of pure light petroleum.[1]

TABLE VII

	Movement in mm.
Alumina (Merck), slightly hydrated	18·5
,, ,, , average sample	5·5
,, ,, , heated 3 hours/230°	3·5
,, ,, , deactivated with methyl alcohol	750
,, ,, , de-activated, then heated 3 hours/230°	5·0
,, ,, , activated with lime water, heated 3 hours/230°	4·0
,, ,, , *nach Brockmann*	8·0
,, from hydroxide heated 3 hours/230°	8·0
,, ,, ,, ,, 15 hours/230°	1·5–2·0
,, ,, ,, ,, 3 hours/600°	2·5
Fuller's earth, old sample	625
,, ,, , heated 3 hours/230°	8·0
Zinc oxide (Merck)	1250
,, ,, ,, , heated 3 hours/230°	18

The alkalinity of the alumina which may sometimes prove troublesome can be reduced by washing with acetic acid. Deactivation of alumina may be attained by washing with methyl alcohol and drying in air. Traces of other substances on the adsorbent may have a great effect on its behaviour.

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[1] Vetter in Bottgers, *Physik. Methoden d. Anal. Chem.*, 1939, III, 1 ; Cook, *Chromatographical Analysis*, Roy. Inst. of Chemistry, Lond., 1940.

It is found, for example, that when copper sulphate is percolated through alumina the copper is retained, but sulphate passes into the filtrate as sodium sulphate: the alumina must have contained a small amount of sodium aluminate to provide sodium ions. Alumina free from sodium does not adsorb copper.

Calcium hydroxide can be made in a suitable form from commercial calcium oxide by slaking with just enough water to make it fall to a powder, and then sifting this through a 120- or 180-mesh sieve. The product should be protected from the air, and should be well shaken before use, to mix the top layer with the main bulk. Calcium carbonate is used as a mild adsorbent and many other substances such as bleaching powder, fuller's earth, kaolin, silica gel, &c., have been used to a limited extent. Many other various adsorbents have been used, including iron hydroxide, zinc hydroxide, stannic acid, silica gel, lead phosphate, barium sulphate, asbestos, talc, filter-paper, &c. Organic adsorbents include tri-stearin, cholesterol, sugars, casein, fibrin, wool, and silk. In some cases it is found convenient to use two or more adsorbents in the same tube, for example, a column of calcium carbonate over one of aluminium oxide, or the above two with a column of sucrose on top. Alumina and most other adsorbents must be extruded from the tube in a condition which is neither too dry nor too moist, if it is to be obtained in the form of a firm coherent cylinder. Strain [1] gives a list of adsorbents arranged in the approximate order of their adsorption capacities, which list is reproduced in Table VIII.

TABLE VIII

Least Active
1. Sucrose, starch
2. Inulin
3. Magnesium citrate
4. Talc
5. Sodium carbonate
6. Potassium carbonate
7. Calcium carbonate
8. Calcium phosphate
9. Magnesium carbonate
10. Magnesia (Merck)
11. Lime (fresh, and partly slaked)
12. Activated silicic acid
13. Activated alumina, and charcoal

Most Active
14. Fuller's earth

Strain points out that the order in this list must be regarded as only a useful guide in the selection of materials for Tswett columns, and that too literal an interpretation must not be placed on it. The activity of an adsorbent must be considered in relation to the chemical nature of the substance under examination, and the solvents used for solution, development, and elution. The order of adsorptive capacities may possibly change with the solute or solutes, and the nature of the solution.

Solvents and Eluents. The choice of solvent for depositing the solute, for developing, or for eluting is dependent on the following fact that as the polarity of the solvent decreases, the more firmly the substance adheres to the adsorbent. Hence solvents with strong polar groups are excellent as eluents, while adsorption takes place most easily from non-polar solvents. Strain [2] has conveniently tabulated a list of solvents arranged in the approximate order of ease of adsorption of solute (Table IX). In using this table a solvent near the top of the table should be chosen for dissolving the original substances. When developing, the same solvent or one slightly lower down should be chosen. Finally, for eluting, a member towards the end of the list should be selected. Thus the following may be accepted as a typical example: Original solution made up in petroleum ether, chromatogram formed, developed with benzene and zones eluted with ethyl alcohol. By suitable combination of solvent and adsorbent a close fractionation of the most complex mixtures may be attained, in many cases preliminary experiments will be necessary.

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[1] *Chromatographic Adsorption Analysis*, 1942.

[2] *Loc. cit.*

TABLE IX

Most Easily Adsorbed

1. Petroleum Ether (B.P. 30-50)
2. „ „ (B.P. 50-70)
3. „ „ (B.P. 70-100)
4. Carbon tetrachloride
5. Cyclohexane
6. Carbon disulphide
7. Ether (alcohol free, anhydrous)
8. Acetone (alcohol free, anhydrous)
9. Benzene
10. Toluene
11. Organic acid esters
12. 1 : 2, di-chlorethane, chloroform, di-chlormethane
13. Alcohols
14. Water (variations with changes in *p*H and salt concentrations)
15. Pyridine
16. Organic acids

Least Easily Adsorbed

17. Mixtures of acids or bases with water alcohol, or pyridine.

Increasing Polarity ↓

Preparation of the Column. The greatest care must be taken to ensure that the column is uniformly and well packed: particularly close packing at the edges must be secured in order to counter the tendency of the solution to pass down more rapidly in this region than in the centre, with the consequent formation of zones having an upper surface which is concave instead of flat. The following are two methods of preparing the column, either of which may be chosen. The porcelain plate with its cover of cotton-wool is first put in position and the adsorbent is sieved immediately before use. Clamping the tube vertically a little of the adsorbent may be added, this is then packed by tapping with a pestle made of hard wood and slightly dished at the centre, the pestle is raised about 6 cm. for each tap, and particular attention is paid to the edges.; a little more adsorbent is added and the process of tapping repeated, and so on until all the adsorbent is added, and the tube is about three-quarters full. When the last layer has been added, attach the tube to the filter flask and start the pump, and continue the tapping on the top surface especially at the edges: finally a small disk of filter-paper, which has been moistened with the solvent, is placed at the top of the column. When two adsorbents are used in the same column, the lower is placed in position as described, a piece of clean linen is wrapped around the head of the pestle and when the top surface has been tapped with the tap on, any adherent particles of adsorbent are carefully wiped from the upper part of the glass tube before commencing the addition of the second adsorbent. The second method consists in preparing a slurry with the adsorbent and the solvent: the tube is placed in a filter flask and connected to a suction-pump, the porcelain plate with its cover of cotton-wool is inserted in the tube and about 10 ml. of solvent added. The slurry is now poured down the tube, the adsorbent is allowed to settle, very slight suction is created and more slurry is added. By keeping a head of solvent above the surface of the adsorbent, and by tapping gently with the pestle, a satisfactory column will be obtained.

Addition of Solution and Subsequent Development and Elution. The suction is again created, and the solution is introduced from the tap-funnel at such a rate that the whole of the column is moistened as rapidly as can be done without disturbing the uppermost layer; as soon as a free layer of solution is formed at the top of the column, the tap-funnel is closed to such an extent, so as always to maintain a small constant ‘ head ’ of solution above the top of the column. When all the solution has been added, development is carried out with large quantities of pure solvent (or some other solvent) until the desired separation of zones has been attained. When the solvent comes in contact with the adsorbed layer, partition occurs between the surface and the solvent; when the solution so formed reaches a free surface, or one containing a less strongly adsorbed substance, deposition or displacement occurs; this results in an increase in the depth of the adsorptive zone of each substance, and frequently in the formation of clear or empty zones between the zones of adsorption, thus facilitating separation. It may happen that a substance is so strongly adsorbed that washing with the solvent produces no effect: in such cases it is necessary to develop with more polar solvents. When development is complete, the suction is prolonged, until the column has reached the degree of dryness which experience shows to be desirable; as has been said, if too dry it will fall to powder easily. The suction is released, the tube is removed and held horizontally, with the upper end over a sheet of plain or glazed paper, and with the aid of a pestle the column is extruded. The column has now to be dissected: for this purpose a scalpel is used and the unloaded portions of the column are first removed; each coloured zone is then carefully scraped with the scalpel; it is not advisable to try to cut the sections straight across because the sections are frequently cupped in form, and often the edges are not regular. On the other hand, as has already been stated, the zones can be scraped out of the glass tube with a glass rod suitably bent at one end. The scrapings are collected, any large pieces crushed to powder and added to the eluent, this slurry is then slightly heated, stirred, and when all the substance is judged to have gone into solution, it is filtered through sintered glass. In some cases elution may be difficult to effect, boiling with ethyl alcohol is very helpful in lixivating the adsorbate. An extreme case may be stated: when the adsorbate is held so tenaciously by calcium hydroxide that it cannot be eluted; the column is powdered and suspended in water, through which carbon dioxide is bubbled to convert the calcium hydroxide to calcium carbonate; elution is then easy (Toth, unpublished work). Another example has already been discussed: higher fatty acids adsorbed on magnesium oxide; the different parts of the column were dissolved in hydrochloric acid—magnesium chloride formed (soluble), and the fatty acids were extracted by shaking with di-ethyl ether. An alternative method to that of cutting up the column is to continue the development until the lowest layer arrives at the bottom of the column, the filtrate is now collected in a clean container, when the whole of this layer has passed into the receiver, the latter is changed and the next zone as it goes into solution is collected ; a repetition of this process will yield fractions containing substances adsorbed in other zones. (It may be necessary to change the solvent, to enable the zones to travel faster down the column.)

SECTION 6: MICRO-CHROMATOGRAPHY.

Many of the ordinary chromatography methods can be adopted for use with small amounts of material.[1]

When the quantity of material available for examination is of the order 0·5 to 1 mg. corresponding small adsorption tubes may be employed. Becker and Schopf[2] used a thick-walled capillary tube of internal diameter of 1 mm. To enable the easy introduction of the solution, a glass tube 4 to 5 mm. in width is fused to one end of the capillary; the other end of the capillary is expanded slightly to take a small plug of cotton-wool. The tube is placed in an adapter which as before is inserted in a suction flask; after the experiment, the tube itself is cut into sections, and the zones eluted. The separation of very small amounts of mixed sugars by Reich has already been discussed, a description of his apparatus will, however, be given here:

70 grams of pure precipitated silica are mixed with 300 ml. of a solution of 25 per cent of pure benzene in dry petroleum (B.P. 60–80). The mixture is kept for about 30 minutes. The adsorption column is prepared thus: part of the mixture is poured into a tube 30 mm. in diameter and 400 mm. high. On the bottom of the tube is placed a wad of cotton-wool and, on this, a disk of porcelain. A pressure is established by compressed nitrogen from the top of the tube, and the liquid filtered through the column of silica until only a few millimetres of liquid remains above the surface of the silica. At this stage a fresh quantity of the mixture is poured into the tube and the filtration continued. This is repeated until the column acquires a height of about 300 mm., when a second perforated porcelain disk is placed at the top of the column, and about 100 ml. of the benzene petroleum-mixture (25 : 75) is filtered by pressure through the column, so that the latter is made compact and homogeneous before beginning the chromatographic adsorption. During this operation, as during the entire procedure, the column must never become dry. The pressure of the nitrogen is regulated during the formation of the column so that the liquid filters through the column at a speed of 6–10 ml. per minute. A speed of 3–4 ml. per minute is used during the adsorption and development of the chromatogram. The esters are recovered by elution, the adsorption is selective and with two adsorptions the separation of the mixtures of the esters is possible.

Crowe[3] employed a different method. A number of adsorbents are placed in the cups of a 'spot plate' or cupped porcelain. A very small quantity of adsorbent in the powdered form is placed in the cup and moistened with various solvents. A drop or two of the solution to be investigated is then placed at the rim of the cup and allowed to flow into the adsorbent, the combination that is most suitable for the particular substance is determined. A Petri dish, quarter-full of the chosen adsorbent, is gently shaken in a tilted position so that the adsorbent settles in the form of a wedge very thin at the upper edge and a few millimetres thick at the lower edge. The solution to be analysed is dropped from a 1-ml. pipette into the centre of the Petri dish which is held in a tilted position so that the solution may flow gently towards the thin edge of the wedge and then filter slowly downwards through the adsorbent. The solvent is added drop by drop to form broad zones of separated material.

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[1] *Cf.* Willstätter and co-workers, *Ber.*, 1922, *55*, 3611, 1924, *57*, 1491.

[2] *Ann.*, 1936, *524*, 124.

[3] *Ind. Eng. Chem. Anal.*, 1941, *13*, 845.

Ion Exchange in Flowing Chromatography. An adsorption apparatus suitable for the separation of organic substances, e.g. aspartic and glutamic acids in micro amounts, has been devised by Drake.[1] In the method an ion exchange resin is used in flowing chromatography. The main features of the apparatus are, a syringe to force the solution through the adsorption column, from which a flexible canula and a capillary-drop tip convey the eluate to a rotating metal drum, on which a filter paper is fastened. The drop tip is pushed along the lowest generatrice of the cylinder and at regular intervals lifted up to the paper, where a drop of the eluate is deposited. The paper can be either used directly, when dyes are analysed ; or prepared in advance with some reagent which, during the run or after some special treatment, gives a colour with the eluted substances ; or afterwards sprayed with a suitable reagent solution. After development, if this is needed, the colour intensities of the spots are compared subjectively with each other and with spots obtained from solutions of known concentration.

After absorption from an aqueous solution of the two acids (on a column of the ion exchange resin ' Amberlite IR-4 '), it was found that both of the acids were eluted with N-hydrochloric acid at a high rate. The best results were obtained with acetic acid. In a concentration of 0·05 per cent a satisfactory separation is obtained.

[1] *Nature*, 1947, *160*, 603.

SECTION 7 : INORGANIC CHROMATOGRAPHY

Inorganic Separations. The possible application of chromatographic methods to inorganic separations was first recommended by Lange and Nagel,[1] who pointed out that this method differed from crystallization from the fused condition, or from solution, in that the attractive forces between solute and solid adsorbent are employed in chromatographical analysis, while in the other case the attractive forces between the solid to be isolated and the solvent are employed. Lange suggests that the former differences are greater than the latter and quotes the isolation of the inert gases by adsorbing other gases on charcoal.

Methods. Alumina and dehydrated aluminium hydroxide can be used as adsorbents. In previous experiments the Hesse micro-tube (already described) was used ; the adsorbent is heated to 70°, cooled, and added in the form of a thick slurry in water, suction is created and with the help of the wooden spatula tight packing is attained. The solution under investigation is added as usual, and the column is washed with water. Zones cannot always be easily differentiated and ‘ development ’ with an appropriate reagent has to be effected. Thus the detection of heavy metal ions is facilitated by ‘ development ’ with ammonium sulphide. Similarly ferricyanide or chromate zones can be rendered ‘ visible ’ by use of silver nitrate solution. Chromatography, as a method of analysis in Inorganic chemistry, is well illustrated by the work of Taylor and Urey,[2] who effected a separation of the isotopes of lithium ; the columns used were 30, 35, and 100 ft. long, and carried 2, 4, and 13 kg. of adsorbent respectively. Towards zeolites, the alkali and akaline earth metals fall into a lyotropic or Hofmeister series, according to the strength with which they are held: $\mathrm{Mg} < \mathrm{Li} < \mathrm{Ca} < \mathrm{Na} < \mathrm{Ba} < \mathrm{NH_4} < \mathrm{K} < \mathrm{Rb} < \mathrm{Cs} < \mathrm{H}$. Hence any metal later in the series than Lithium would displace it ; using a zeolite as adsorbent it would be possible then that a separation of lithium isotopes could be attained. Experimentally, lithium chloride was introduced and the column then washed with sodium chloride solution. The fractionation was unmistakable and showed that Li^6 is preferentially retained by the zeolite.

Selective Adsorption. Karagunis and Commulous[3] report the development of a new method for the resolution of a racemic compound by selective adsorption. The method is based upon the different degree of adsorption which an optically asymmetric crystal, such as *d*- or *l*-quartz, shows for two antipodes. The result of this selective adsorption is that when a *dl*-solution is passed through a Tswett column, the *d*- and *l*-component are separated and located at different heights. They used quartz powder prepared from *d*- and *l*-quartz crystals, as the asymmetric adsorbing medium, and a solution tri-ethylene diamine chromi-chloride as the racemic compound. The apparatus they employed is shown in Fig. 15 (XIV^3). After activating the adsorbing medium by heating *in vacuo*, they allowed

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[1] *Z. Electrochem.*, 1936, 943.

[2] *J. Chem. Phys.*, 1938, *6*, 429.

[3] *Nature*, 1938, *142*, 163.

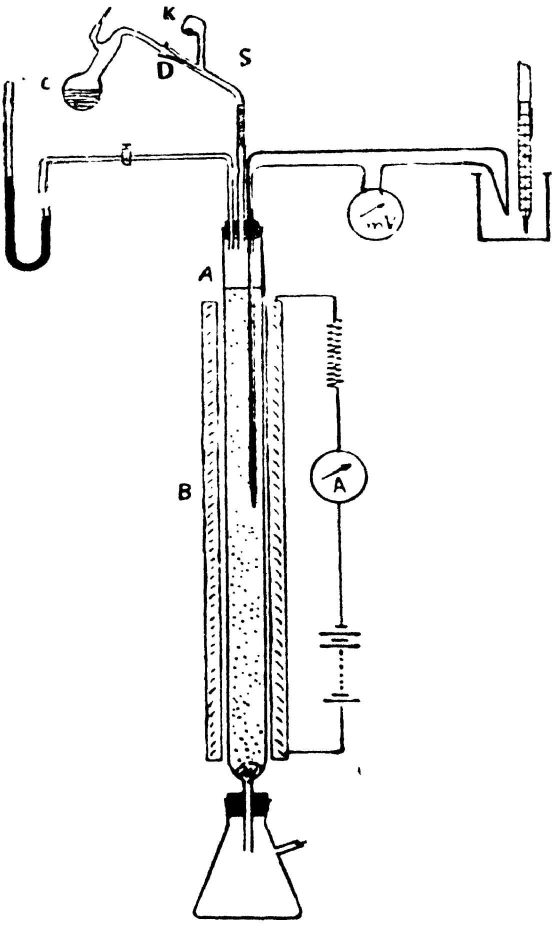

FIG. 15 (XIV^3)
Selective adsorption apparatus of Karagunis and Coumoulos

the racemic solution to pass through the column A of the quartz powder by breaking the glass end S by the metal sphere K and tipping up the vessel C. The filtrate and the solutions obtained by successive elutions of the adsorbed salt by 85 per cent alcohol were examined in the polarimeter. The table appearing on the next page indicates that the solutions obtained were optically active :

TABLE X

Adsorbing medium	1	2	3	4	5
	α_D	α_D	α_D	α_D	α_D
l-quartz	− 0·023	− 0·041	+ 0·020	+ 0·108	—
l-quartz	− 0·058	− 0·121	− 0·018	+ 0·046	+ 0·034
d-quartz	+ 0·023	− 0·020	− 0·050	—	—

By using *d*-quartz the first elutions are dextro-rotary and the next solutions are laevo-rotary. By using *l*-quartz the opposite occurs, thus the conclusion that the asymmetric quartz surface adsorbs more strongly the antipode of the opposite sign. The extension of this method would greatly facilitate and simplify the difficult task of separating both organic and inorganic optical isomers.

Karagunis and Coumoulos [1] claim the partial resolution of a complex chromium salt by the use of active quartz. Following up the work of Tsuchida, Kobayashi and Nakamura [2] upon the detection of a racemic inorganic complex by immersing powdered active quartz in its solution, the possibility of extending these results by the use of quartz columns in conjunction with inorganic as well as organic complexes has been examined by Henderson and Rule.[3]

Strain [4] has described the separation of coloured water-soluble organic substances, such as nitro-, hydroxy-, amino-, azo-, carboxy-, and sulphonic-compounds from mixtures, by a combination of electrophoretic and chromatographic adsorption methods. The method is as follows: an electrode of coiled wire covered loosely with cotton is placed in the constricted end of a glass tube and the tube is filled with the adsorbent usually Hyflo Super Cel (heat-treated siliceous earth) or mixtures of this with talc. Before use, the adsorption column is attached to a suction flask and filled with water. A little of the mixture of charged or ionized coloured substances is then drawn into the upper part of the column where it forms a homogeneous coloured band. The suction is released; a second electrode is placed at the top of the column and covered with water and potential is applied to the two electrodes. This causes the pigments to migrate towards the electrode of opposite charge and gives rise to a series of coloured zones each of which contains a single pigment. Compounds separated upon adsorption columns by electrophoresis may be isolated in two ways. The bands of coloured substances may be removed separately from the column and the pigments themselves eluted from the adsorbent with additional water, ethyl alcohol alkalies or acids; alternatively the pigments may be washed through the columns and collected separately in successive portions of the percolate. Strain [5] states that the width of the bands of adsorbed substances formed in the columns by electrophoresis depends upon the quantity of pigment present and upon the adsorptive capacity of the adsorbent. In experiments carried out at room temperature with large columns, the bands of pigments always exhibit well-defined boundaries throughout the mass of the adsorbent. The adsorbent thus serves to prevent mixing of the coloured substances as well as to aid in their separation.

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[1] *Nature*, 1938, *142*, 162.

[2] *Chem. Soc. Japan*, 1935, *56*, 1339.

[3] *Nature*, 1938, *142*, 163.

[4] *J. Amer. Chem. Soc.*, 1939, *61*, 1292.

[5] *Loc. cit.*

A pronounced electro-osmotic effect was observed in all experiments carried out thus far. Since the water usually moves towards the cathode this electrode was placed at the top of the column so that the head of water could be adjusted to balance the electro-osmotic pressure. The mixtures Strain [1] separated by this method (the first named in each group remaining nearest the cathode) were: aminoazobenzene and indigo carmine; 3.nitro-4-aminoanisole and indigo carmine; methyl orange and methyl red; methyl orange and 2.6.di-chlorophenol indophenol; methyl red and indigo carmine; picric acid and methyl orange. For separation of these compounds potentials ranging from 175 to 200 volts and currents from 0·5 to 2 milliamps were used with columns ranging in size from 2 × 13 cm. to 3 × 23 cm. The quantity of each pigment adsorbed varied from 2 to 15 mg.

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[1] *Loc. cit.*

CHAPTER XV[3]

COLLOIDS *

SECTION 1: THE NATURE OF COLLOIDS

THE term 'colloid' was introduced by Graham in 1861 to signify substances such as gums, starch, proteins, &c., which are difficult to crystallize, which diffuse slowly in water, and which are not readily able to pass through certain membranes, e.g. parchment, pig's bladder (see 'Dialysis'). Substances which readily crystallize, which diffuse relatively rapidly, and which readily pass through membranes he termed 'crystalloids'. The modern interpretation of the term 'colloid' differs from that of Graham's time inasmuch that nowadays it is recognized that the colloid 'state' is one which all kinds of chemical material can assume under suitable conditions. Colloid systems are dispersions which contain one substance (the disperse (dispersed) phase)[1] distributed in another substance (the continuous (dispersion, external) medium), where the dispersed particles have dimensions defined very approximately as lying between 1 mμ and 500 mμ (*N.B.* 1 mμ = 10^{-7} cm.) It is thus seen that the upper limit of this dimension-range coincides approximately with the lower limit of the range of microscopic vision.

The various kinds of disperse systems, as originally classified by Ostwald, are indicated in the following table:

Disperse phase	Dispersion medium	Contraction	Example
Solid	Solid	S/S	Alloys. Gold in ruby glass
Solid	Liquid	S/L	A hydrosol of gold
Solid	Gas	S/G	Smokes
Liquid	Solid	L/S	Minerals with occluded liquids
Liquid	Liquid	L/L	Emulsions
Liquid	Gas	L/G	Fog. Mist
Gas	Solid	G/S	Porous solids, e.g. pumice stone
Gas	Liquid	G/L	Froths and foams
Gas	Gas	G/G	No example, owing to complete miscibility of all gases

The S/L and L/L types have been most investigated.

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* The section on Colloids in the second volume has been completely revised and extended considerably in this supplementary volume. Emulsions are now given a separate chapter. This work has been undertaken by Dr. J. C. Aherne. The authors wish to express their indebtedness for this co-operation.

[1] For a discussion as to whether colloid systems should be regarded as 'one-phase' or 'two-phase' see chapter by Buchner in Alexander's *Colloid Chemistry*, New York (1926).

The definition of the colloidal state has been extended, notably by Ostwald and von Buzagh, to include certain systems (' difform systems ') in which occur ' discontinuities ' of colloidal dimensions. Thus a solid film (effectively two-dimensional) of a higher fatty acid on a water surface, separating the water from air, constitutes a discontinuity which, although it cannot be termed a dispersion, has a thickness falling within the colloidal range. Such a difform system is of the liquid-film-gas variety. It is possible to collect such films on metallic surfaces so as to obtain a difform system of the solid-film-air variety.

In addition to the systems already given, mention may be made of macromolecular substances (e.g. plastic resins resulting from the polymerization or polycondensation of simple molecules) in which the colloidal attributes (such as ability of dispersions to gel, thixotropy, &c.) often result from the actual size of the macromolecule. Thus macromolecules of the linear variety (linear ' polymers ') may also have sizes falling within the colloidal range. The solutions of these highly-polymerized materials are, however, often ' true ' molecular solutions.

Ordinary colloidal dispersions are often termed ' sols ' and, broadly considered, sols may be subdivided into two categories, viz. (*a*) ' suspensoid ' (' lyophobic ',[1] ' hydrophobic ',[2] ' irreversible ', ' unstable ' [3]) sols and (*b*) ' emulsoid ' [4] (' lyophilic ', ' hydrophilic ', ' reversible ', ' stable ') sols. It is customary to regard a gold sol as being typically suspensoid and a gelatine sol as being typically emulsoid. The following table indicates some characteristics in which these typical sols resemble each other and certain characteristics in which they differ :

Suspensoid sols (e.g. gold sol)	Emulsoid sols (e.g. gelatine sol)
Cannot be obtained by direct ' solution '	May be obtained by direct ' solution '
High ' molecular ' weight and low rate of diffusion	High ' molecular ' weight and low rate of diffusion
May be purified by dialysis	May be purified by dialysis
Particles charged electrically	Particles frequently, but not necessarily, charged electrically
Coagulate after prolonged dialysis. Presence of small amount and certain kind of electrolyte essential for permanence of sol system	Usually no change on prolonged dialysis
Stable only when dilute. Sensitive to addition of traces of electrolytes. Coagulation (to coarse granules) irreversible	Stable even when concentrated. Insensitive to addition of traces of electrolytes. May be ' salted out ' only when added electrolyte is in relatively high concentration. Reversibly precipitated and dissolved

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[1] The terms lyophobic (Gr. ' fear to loosen ') and lyophilic (Gr. ' love to loosen ') have, in the study of colloid systems, assumed the meanings ' solvent hating ' and ' solvent loving ' respectively.

[2] Hydrophobic = ' water hating ' ; hydrophilic = ' water loving ' ; i.e. where the dispersion medium is aqueous.

[3] The terms ' unstable ' and ' stable ' were introduced to indicate the difference in behaviour towards electrolytes.

[4] The term ' emulsoid ' was chosen to indicate certain resemblances in their properties to the characteristics of the coarser emulsions.

Suspensoid sols (e.g. gold sol)	Emulsoid sols (e.g. gelatine sol)
Often coloured and display evidence of optical heterogeneity	Often colourless and optically almost homogeneous
Low viscosity. Dispersed particles unsolvated	Dispersed particles highly solvated, hence systems usually have relatively high viscosity [1]
Material to be dispersed does not swell in contact with the ' solvent '	Material to be dispersed usually swells in contact with the ' solvent ' before dissolving
The sols exhibit phenomenon of electrophoresis	The sols may or may not exhibit the phenomenon of electrophoresis
Systems do not gel	Systems often gel
Surface tension substantially equal to that of the pure solvent	Surface tension lower than that of pure solvent
Unable to yield persistent froths on being shaken	Generally yield fairly persistent froths on being shaken

The particles in a lyophilic sol may be represented as in Fig. 1 (XV^3). ' Intermediate ' sols are also known, e.g. certain hydrosols of the oxides of silicon and chromium. They have, in general, the following characteristics :

Less sensitive to electrolytes than typical hydrophobic sols, but more sensitive than hydrophilic sols. Surface tension substantially the same as that of the dispersion medium, but viscosity somewhat greater. Show the phenomenon of electrophoresis, and a faint Tyndall effect. Coagulate after prolonged dialysis. Presence of a certain amount and kind of electrolyte essential for the permanence of the sol system. Upon evaporation of the fluid, the residue may be redispersed in a fresh quantity of the solvent if the original sol was not of high purity and if not thoroughly dried. Conversely, if the sol was very pure and was thoroughly dried the residue cannot be redispersed (denoting irreversibility of the process of obtaining the residue).

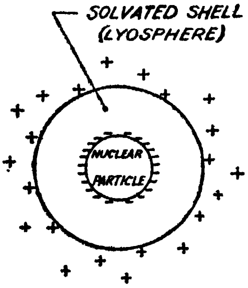

FIG. 1 (XV^3)
Particle in a lyophilic sol

A ' hydrosol ' is a sol in which water is the dispersion medium. The general term ' organosol ' is used to describe any dispersion in which an organic liquid is the dispersion medium ; when alcohol is the dispersion medium the particular term ' alcosol ' is usually used. A ' monodisperse ' sol system is one in which the particles of the dispersed material are of uniform size (the terms ' homodisperse ' and ' isodisperse ' are also employed synonymously), while a ' polydisperse ' sol system is one which contains particles of the dispersed material of different sizes.

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[1] The viscosity of a suspensoid sol, like many other physical properties of such a system, is more or less an additive function (i.e. sum of properties of component parts). See, under ' Emulsions ', the Einstein equation for viscosity. The relationship holds fairly well for suspensoids, although particle-size is often a consideration, and in many cases the viscosity does not vary linearly with the concentration.

'Solvation' means chemical combination of ions, molecules, or aggregates of a 'solute' with molecules of the 'solvent'; when the solvent is water the term 'hydration' is employed.

A 'lyosphere' is an adsorption layer which forms at the surface of an adsorbent from the liquid which is in contact with the adsorbent material. Lyospheres are diffuse layers of liquid extending sometimes far beyond molecular dimensions.

The term 'micelle' was suggested by Nägeli to describe crystal-like aggregates which fall within the range of colloidal dimensions. Duclaux suggested that a micelle would consist of three constituent parts, viz. (1) a particle, (2) ions of one kind of charge adhering to the surface of the particle, (3) gegenions (i.e. 'dissociated' ions of the opposite kind of charge constituting the outer (diffuse) layer). In accordance with this suggestion the micelles in a positive silver bromide sol would, in the presence of the excess silver nitrate, be somewhat as represented in Fig. 2 (XV^3), while the micelles in a negative silver bromide sol would, in the presence of the excess potassium bromide, be constituted as in Fig. 3 (XV^3). McBain favoured the term 'ionic micelle' to describe hydrated aggregates of neutral soap molecules and fatty acid ions occurring as 'giant' polyvalent ions in moderately concentrated soap solutions. These ionic micelles may be represented by such formulae as:

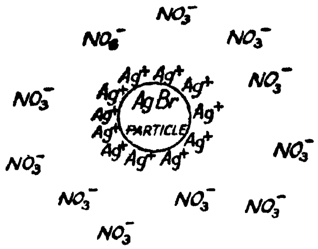

FIG. 2 (XV^3)
Micelle in positive silver bromide sol

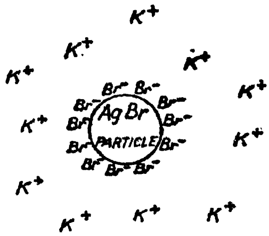

FIG. 3 (XV^3)
Micelle in negative silver bromide sol

$$(Na\bar{P})_x(\bar{P}')_n(H_2O)_m,\ (Na\bar{P})_x(H\bar{P})_n(OH')_n(H_2O)_{m-n},$$

$$(Na\bar{P})_{x-m}(NaH\bar{P}_2)_n(OH')_n(H_2O)_{m-n}$$

where $\bar{P}$ stands for the palmitate radicle. The balancing sodium ions (contra-ions) are in the liquid close to the ionic micelle.

A sol of 'ferric oxide' (prepared (*a*) by digesting freshly precipitated and washed ferric hydroxide with concentrated ferric chloride solution (peptizing agent) followed by dialysis, or (*b*) by the hydrolysis which occurs when a few millilitre of ferric chloride is added slowly to much boiling water (followed by dialysis) has been represented in various ways, e.g. as in Fig. 4 (XV^3) (where the symbolic representation does not indicate a chemical compound but an agglomerate of several compounds), and in Fig. 5 (XV^3). Pennycuick suggested the formula represented in Fig. 6 (XV^3) for the micelle in a platinum sol made by dispersing platinum in water by the Bredig method.

Nowadays the term micelle is popularly used to represent in general the particles of the dispersed phase, including the compensating double layer, while the dispersion medium is often referred to as the ‘ intermicellar liquid ’.

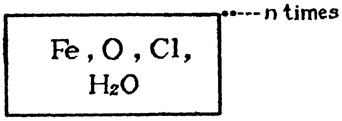

FIG. 4 (XV³)
Micelle in sol of ‘ ferric oxide ’ (one representation)

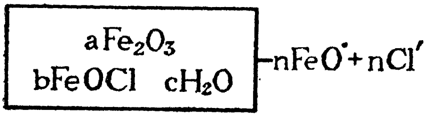

FIG. 5 (XV³)
Micelle in sol of ‘ ferric oxide ”
(a second representation)

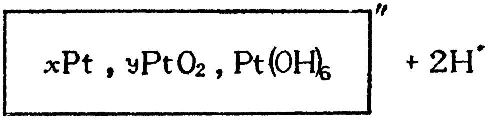

FIG. 6 (XV³)
Micelle in platinum sol

Precipitation. ‘ Coagulation ’ means the aggregation of numbers of the dispersed particles in a colloid system into larger particles with the characteristics of a precipitate or of a ‘ true ’ suspension. The phenomenon is occasioned by the breakdown of factors originally responsible for the preservation of the sol system (for example, by removal of the electric charge). The term ‘ flocculation ’ is often used synonymously with the foregoing, although it is particularly appropriate in the case of solid suspensions owing to the characteristic ‘ floc ’ nature of the aggregates. The term ‘ salting out ’ describes in particular the process of the precipitation of hydrophilic colloids by electrolytes. A relatively large quantity of an electrolyte is needed to accomplish the ‘ salting out ’ owing to the relative indifference of these colloid systems to added electrolytes. The actual ‘ salting out ’ is the result of two processes (see p. 340). In the cases of hydrophobic colloids, which are very sensitive to electrolytes (relatively small quantities), the term ‘ salting out ’ is not used in describing the flocculation. ‘ Gelatinization ’ (‘ gelation ’) refers to the process of the formation of precipitates which have the characteristics of a gel (*q.v.*). If a sol be coagulated by a sufficiently low concentration of electrolyte it may be possible to follow experimentally the process of aggregation.

‘ Slow ’ and ‘ Rapid ’ Coagulation. If a small quantity of an electrolyte, e.g. sodium chloride, be added to a red ‘ gold sol ’ (a hydrophobic sol), the colour of the sol changes gradually to violet and then to blue, due to coagulation of the particles. The reciprocal of the time taken for the complete colour-change may be considered as one measure of the rate of coagulation. Up to a certain limit the greater the quantity of electrolyte added the greater the rate of coagulation, but above this limit the rate of coagulation is more or less constant, i.e. it does not increase with further increases in the concentration of the electrolyte. This is borne out by some of Zsigmondy's results as illustrated in Table I. A distinction is therefore made between the range of 'slow' coagulation and the range of 'rapid' coagulation of hydrophobic sols. The rate of rapid coagulation is uninfluenced by the nature of the added electrolyte. It is probable that in the range of rapid coagulation the forces of electrical repulsion due to the electrical double-layer are greatly diminished or even completely removed. Smoluchowski,[1] using the law of probabilities and assuming the particles to be uncharged and that all the collisions are fruitful (i.e. absence of elasticity), showed that in the case of rapid coagulation of a hydrophobic sol if there were n_0 primary ('single') particles per unit volume at the commencement and if, after a time t, there were in unit volume n_1 of these 'single' particles, n_2 'double' particles, n_3 'treble' particles . . . n_k particles each consisting of an aggregation of k 'single' particles, the following relationships hold:

TABLE I

Concentration of added electrolyte (millimols per litre)	Time of Coagulation (in seconds)	
5	150	Range of 'slow' coagulation
10	12	
20	7·2	Range of 'rapid' coagulation (tolerably constant)
50	7	
100	7	
150	6	
500	7	

$$n_1 = \frac{n_0}{(1 + \alpha n_0 t)^2}$$

$$n_2 = n_0 \frac{\alpha n_0 t}{(1 + \alpha n_0 t)^3}$$

$$\ldots \quad n_k = n_0 \frac{(\alpha n_0 t)^{k-1}}{(1 + \alpha n_0 t)^{k+1}}$$

After a time t the grand total of the numbers of particles of all different sizes would be

$$\Sigma n = \frac{n_0}{1 + \frac{t}{T_1}}$$

where $\alpha = 4\pi DR$, D being the coefficient of diffusion of the particles (mean displacement due to Brownian movement), R being the radius of the sphere of attraction (i.e. the radius of the hypothetical sphere which surrounds every particle in such a way that any other particle whose centre enters this sphere will be firmly retained). T_1 (known as the 'time of coagulation') is equal to $\frac{1}{\alpha n_0}$, and is a convenient measure of the rate of coagulation since when $t = T_1$, $\Sigma n = \frac{1}{2}n_0$, i.e. when the time, t, of coagulation reaches the value T_1, the total of the particles $(n_1 + n_2 + n_3 + \ldots n_k)$ becomes half what it was at the commencement.

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[1] *Physick. Z.*, 1916, *17*, 557 and 583; *Kolloid-Z.*, 1917, *21*, 98; *Z. Physik. Chem.*, 1917, *92*, 129.

In Fig. 7 (XV³) the values of $\frac{\Sigma n}{n_0}, \frac{n_1}{n_0}, \frac{n_2}{n_0}, \frac{n_3}{n_0}, \frac{n_4}{n_0}$ are shown plotted against $\frac{t}{T_1}$. At the commencement of coagulation $(t = 0)$, $\Sigma n = n_0$ and also the number of 'single' (i.e. primary) particles $n_1 = n_0$, so that $\frac{\Sigma n}{n_0} = \frac{n_1}{n_0} = 1$. As the coagulation proceeds, n_1 and Σn continuously diminish, and the number of 'double' particles, in the initial periods of the coagulation, begins to increase to a maximum and then to diminish while the 'treble' particles increase to a maximum, and so on until all the particles have coagulated and settled out. Smoluchowski's equations for rapid coagulation have been verified experimentally by a number of workers, and the observed influence of temperature on the phenomenon is found to be in good agreement with the related equation for Brownian movement (see p. 353):

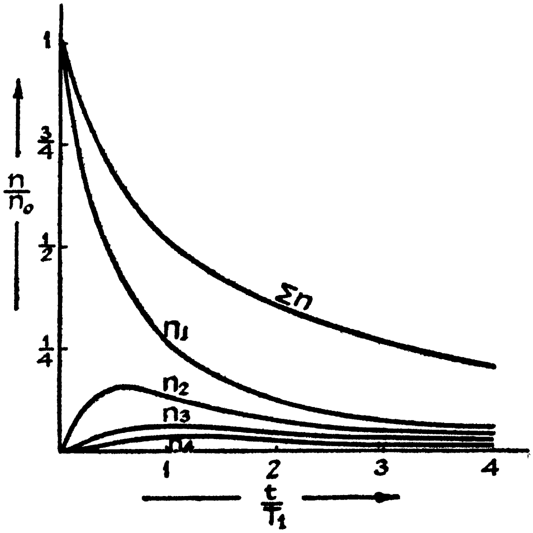

FIG. 7 (XV³)
Smoluchowski's theory of 'rapid' coagulation on a hydrophobic sol

$$D = \frac{RT}{6\pi N\eta a},$$

where R is the gas constant, T is the absolute temperature, N is Avogadro's

Number, η is the viscosity coefficient, and a is the radius of a particle (assumed spherical). For an extension of the theory to the case of polydisperse sols see Müller, *Kolloid-Z.*, 1926, *38*, 1.

The mechanism of 'slow' coagulation (i.e. coagulation caused by relatively small amounts of electrolyte) is more complex. In a discussion on slow coagulation Smoluchowski modified the 'probability of aggregation' formula for rapid coagulation by introducing a factor, ξ, which represents the fraction of the total 'close approaches' which would be fruitful—there should be a reduction in the proportion of fruitful 'collisions' owing to the incomplete subjugation of the double-layers (although even for slow coagulation the ζ-potential may require to be below a certain critical value). The factor ξ depends on the nature and concentration of the electrolyte. Complications arise in the experimental testing of the modified formula owing to difficulty in measuring properly the rate of coagulation. Velocity-curves have been given which suggest that the coagulation is of the autocatalytic type (since the coagulation proceeds at first very slowly, then increases rapidly, and then falls off again). If, however, the experiment is conducted with simultaneous vigorous stirring the 'velocity of coagulation' curve becomes more normal, and evidence of autocatalytic coagulation disappears. The remarkable influence of the concentration of a given electrolyte is reflected in the fact that the constant of velocity is proportional to a high power of the concentration.

If to a given volume of colloidal solution a quantity of electrolyte solution is added sufficient to produce coagulation, and if the concentration of the electrolyte in the mixture of sol and electrolyte be C, then $\frac{1}{C}$ is called the 'coagulative power' of the electrolyte in question for the given sample of colloid (see Liminal Concentration). If several sols of the same colloidal material are used, the results should be compared in terms of the necessary concentration per gram of the dispersed phase per millilitre of the sol.

Attention should be paid to the units in which coagulative power is expressed. Thus if C be taken in milligram-ions of coagulating ion per litre, the coagulative power will be obtained in terms of the milligram-ion, i.e. the 'ionic' precipitating power; if C be expressed in milligram-equivalents of coagulating ion per litre, the coagulating power will be obtained in terms of the milligram-equivalent, i.e. the relative coagulating efficiency per unit charge.

The Hardy-Schulze [1] Rule states that for suspensoid sols the coagulative powers of univalent, bivalent, and tervalent contra-ions stand substantially in the ratio $1 : x : x^2$, where x has a value of about 30. Various experimenters, however, have found ratios different from the foregoing. (*Note.*—A 'contra-ion' is an ion which carries a charge opposite in sign to that carried by the dispersed particles.) The Rule can be regarded as only qualitative.

Freundlich [2] offered one explanation of the valency effect by assuming that for coagulation, (*a*) approximately equal numbers of charges must be adsorbed by a given sol particle, independently of the valency of the coagulating ion (thus if Z_1 units of charge are necessary for coagulation, this would be supplied by the adsorption of Z_1 univalent ions, $\frac{Z_1}{2}$ bivalent ions, or $\frac{Z_1}{3}$ tervalent ions and, for example, the numbers of milligram-ions necessary would also be in the ratio $Z_1 : \frac{Z_1}{2} : \frac{Z_1}{3}$), and (*b*) that all ions follow approximately the same adsorption isotherm (the concentration of the ions being expressed in terms of milligram-ions of coagulating ion per litre). The foregoing hypothesis is illustrated in Fig. 8 (XV^3), C_1, C_2, and C_3 are the respective concentrations of univalent, bivalent, and tervalent ions needed to give rise to the adsorptions Z_1, $\frac{Z_1}{2}$, and $\frac{Z_1}{3}$ of these ions respectively needed to supply the charge necessary for coagulation. It will be observed that C_1 is much greater than C_2 which, in turn, is greater than C_3. The curve in Fig. 8 has an equation of the usual type :

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[1] *J. Prakt. Chem.*, 1882, *26*, 431.

[2] E.g. Working with a sol of mercuric sulphide. See Freundlich and Schucht, *Z. physik. Chem.*, 1913, *85*, 641.

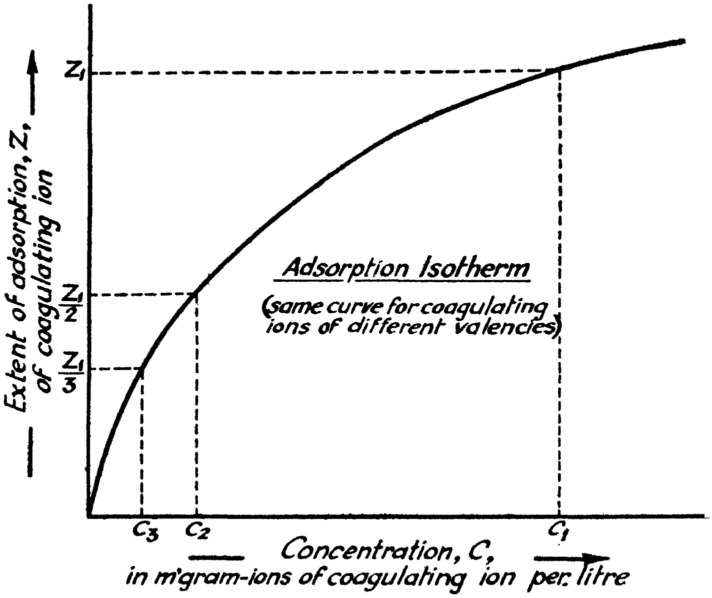

FIG. 8 (XV^3)
Freundlich's hypothesis of valency-effect

$$Z = aC^{\frac{1}{b}}$$

where Z = mass adsorbed per unit mass of dispersed phase, and *a*, *b* are constants for the given colloid.

Although the valency of the precipitating ion has a predominating influence on its ability to cause the coagulation of a suspensoid sol, it is found that even ions of the same valency usually vary somewhat amongst themselves in coagulative power. Thus the orders

$Cs^{\cdot} > Rb^{\cdot} > K^{\cdot} > Na^{\cdot} > Li^{\cdot}$, $Ba^{\cdot\cdot} > Sr^{\cdot\cdot} > Ca^{\cdot\cdot} > Mg^{\cdot\cdot}$, $Cl' > Br' > I'$, have often been observed (see and compare Hofmeister Series). Hydrogen-ions and hydroxyl-ions are usually exceptionally potent when acting as coagulating ions.

Murray[1] gave an equation for the coagulative power of cations :

$$C = kA^d,$$

where C = concentration of a cation needed to effect complete precipitation of a colloid in a given time ; A = atomic number of the element of which the cation in question is the ion ; k = a coefficient the value of which depends on the anion and the colloid ; d = a constant for the given colloid at the particular concentration used. For observations on the effect of colloid concentration upon coagulative powers of electrolytic solutions, *see* Burton and Bishop, *J. phys. Chem.*, 1920, *24*, 701 ; Burton and MacInnes, *ibid.*, 1921, *25*, 517 ; Weiser and Nicholas, *ibid.*, 1921, *25*, 742. The latter authors emphasized the influence of the relative adsorbabilities of precipitating ions (ions of charge opposite to that on the particles) and stabilizing ions (ions of charge similar to those on the particles) upon the liminal values (see p. 346).

Wiegner used the term 'orthokinetic coagulation' to describe the coagulating effect which occurs between falling particles when attracting forces act between the particles.

Two suspensoid sols in which the micelles carry opposite charges precipitate each other (mutual precipitation) when they are mixed in a definite ratio. If a reasonable excess of either of the sols be present no precipitation may occur, and the sign of the charge on the resultant mixture will be the same as that of the sol which is present in excess.

Irregular Series in Precipitation. It has been found that when, for instance, a solution of aluminium sulphate is added to a sol of mastic (a negatively charged sol) there is precipitation in the initial stages of the addition, then peptization of the material as a result of the addition of intermediate quantities, followed by re-precipitation when still larger quantities are added. Such effects, when they occur, are called 'irregular series' or 'abnormal series' in coagulation. To explain the phenomena just described Kruyt suggested that the positively charged aluminium ions (or the alumina) neutralize the negative charge on the mastic micelles, thus causing the first precipitation. The precipitated material is then peptized as a positively charged sol, only to be reprecipitated when, at still higher concentrations, the acquired positive charge is neutralized by the adsorption of negative sulphate-ions. The phenomenon is most commonly encountered with sols consisting of negatively charged micelles, and the effect is most evident when the added salts consist of heavy-metal or polyvalent inorganic cations (or of univalent organic cations) associated with univalent anions. With a positively charged sol, a univalent cation associated with a polyvalent anion has been found most effective. However, positively charged ferric oxide sol has been found to display an irregular series with sodium hydroxide (both ions univalent) on account of the relatively great adsorbability of the hydroxide-ion.

The process of coagulation of lyophilic sols is (*a*) partly one of desolvation

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[1] *Phil. Mag.*, 1920 (6), *40*, 578.

(i.e. removal of the protecting 'bound' solvent (solvent sheath)), and (*b*) partly one of modification of electrical properties. To illustrate parts (*a*) and (*b*) of a coagulation of a lyophilic sol, Fig. 9 (XV^3) is given (taking a hydrophilic sol as representative). If part (*a*) is effected by ions,[1] the effectiveness of different ions follows a Hofmeister lyotropic series (*q.v.*). Part (*b*) (the variation in electrical properties) is, for the ions, approximately governed by the Hardy-Schulze valency rule. In practice, in the coagulation of a lyophilic sol by ions of a particular kind, the position of the ion in the Hofmeister series exercises a more important influence on the process than the value of its valency, i.e. the Hardy-Schulze rule is of less significance.

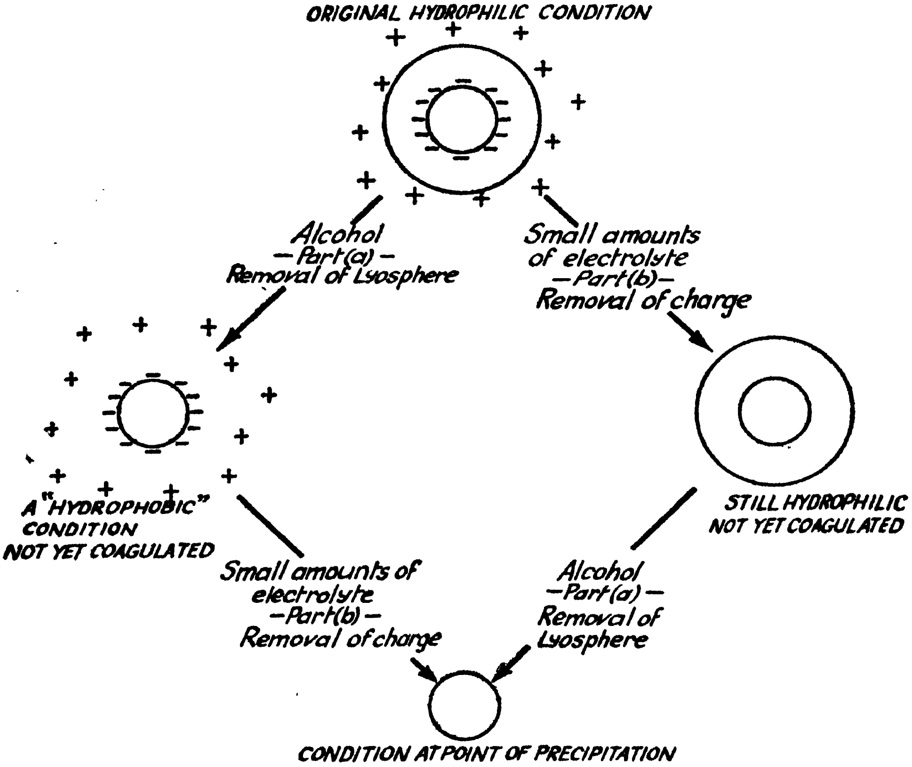

FIG. 9 (XV^3)
Coagulation of a hydrophilic sol

Protective Action and Sensitization. If a sol of the hydrophilic substance gelatine be added to a gold or a silver sol so prepared that it is alkaline in reaction, it is found that, although the physical appearance of the metallic sol remains unchanged, the sol becomes less sensitive (more stable) towards added electrolytes and to evaporation (e.g. sometimes after being taken to dryness the residue may be redispersed in water without difficulty). The decrease in sensitivity is said to be due to 'protective action ', and the sol is said to have been ' protected '. Substances such as gelatine, soap, casein, and gum arabic are accordingly often called ' protective colloids '.

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[1] The lyosphere may be removed by a sufficient concentration of suitable ions.

Protected sols, originally hydrophobic, assume many of the characteristics of the protective colloid. Thus the minimum concentrations of different salts required to coagulate the protected sol are very similar in value to those required to coagulate sols of the protective colloid alone. The Hardy-Schulze rule does not hold even approximately in the case of protected sols, the valency of the precipitating ion having no marked effect. In addition, by the use of a protective colloid it is possible to prepare concentrated sols of materials which normally give lyophobic sol-systems, e.g. in the preparation of colloidal silver sols used medicinally.

In the example already given (alkaline gold sol and gelatine) the charges on the gold particles and on the gelatine are like in sign (both negative).

When it is desired to prepare a protected colloid, the protective colloid is usually added during the preparation of the sol and not after.

It is likely that in the phenomenon of protection a thin film of skin of the protective emulsoidal colloid or a layer of the emulsoidal particles is adsorbed on the particles of the suspensoidal sol thus virtually conferring on the system the characteristics of an emulsoid sol.

In reasonably acidic solution (e.g. $p\mathrm{H} = 4{\cdot}5$) minute amounts of gelatine may cause flocculation of a gold sol, although if greater amounts of the gelatine be added rapidly protection will be the net result. The *p*H-value of the solution is thus often a factor affecting the influence of the added ' protective ' colloid. In the case just quoted the first traces of added gelatine with its positive charge, causes a reduction in the stability of the negatively charged gold sol towards added electrolytes and a reduction in the numerical value of the electrophoretic mobility (p. 442). Such an effect is known as ' sensitization ' of the original sol. Further slight increases in the amount of added gelatine may cause the flocculation, which phenomenon is probably due to normal adsorption of the particles of the gelatine which behave as colloidal electrolytes. Under such conditions the hydrophobic particles are still incompletely coated with adsorbed gelatine films. When, however, the gelatine is originally added in larger amounts, complete protein-films are adsorbed around the gold particles, resulting in reversal of the charge (negative to positive) and a consequent change in the sign of the electrophoretic mobility. The sol assumes the characteristics of an emulsoidal system and the gelatine is now exhibiting its normal protective action.

Zsigmondy pointed out that when the particles of an hydrophobic sol are much smaller than those of the protective colloid the hydrophobic particles are adsorbed by the hydrophilic particles instead of vice versa.

The phenomenon of the sensitization of hydrophilic sols by other hydrophilic sols is also well established, and cases have been recorded in which emulsoid sols have been coagulated by the addition of relatively small amounts of a colloid with a charge of like sign.

U-Number. The ' U-Number ' is a measure of the sensitizing (or the precipitating) power of a colloid. It is given as the number of milligrams of the colloid needed to change the colour of 10 ml. of a gold sol to 100 ml. of which has been added 3·5 ml. of 0·1 N hydrochloric acid.

Iso-electric Point. The iso-electric point is that condition of the dispersion medium (usually registered as a *p*H value) at which there is no potential difference between it and the dispersed phase, i.e. where the electric charge is counterbalanced or neutralized. In the case of a colloid ampholyte (*q.v.*), such as a protein sol, the *p*H-value corresponding to the iso-electric point may be investigated as follows (the assumption being made that the Law of Mass-Action is valid for the dissociation of ionizable materials of colloidal dimensions—an assumption not fully justifiable) :

For simplicity, consider a monacidic monobasic ampholyte such as glycine (CH_2NH_2COOH).

Considered as an acid its ions may be written CH_2NH_2COO' and $H^{\cdot}$, and as a base its ions may be written[1] $CH_2COOH.NH^{\cdot}_3$ and OH'.

For brevity, let the dissociations be written

$$ROH \rightleftharpoons RO' + H^{\cdot} \quad . \quad . \quad . \quad . \quad (a)$$

and

$$ROH \rightleftharpoons R^{\cdot} + OH' \quad . \quad . \quad . \quad . \quad (b)$$

In case (*a*) the dissociation constant of the acidic ionization is given by

$$K_a = \frac{[H^{\cdot}].[RO']}{[ROH]}$$

In case (*b*) the dissociation constant of the basic ionization is given by

$$K_b = \frac{[R^{\cdot}].[OH']}{[ROH]}$$

i.e. $$[RO'] = \frac{K_a[ROH]}{[H^{\cdot}]}, \text{ and } [R^{\cdot}] = \frac{K_b[ROH]}{[OH']}, \text{ hence,}$$

$$[RO'] + [R^{\cdot}] = \frac{K_a[ROH]}{[H^{\cdot}]} + \frac{K_b[ROH]}{[OH']}$$

but since $[OH'] = \frac{K_w}{[H^{\cdot}]}$, where K_w = ionic product of water, then,

$$[RO'] + [R^{\cdot}] = \frac{K_a[ROH]}{[H^{\cdot}]} + \frac{[H^{\cdot}].K_b.[ROH]}{K_w}$$

Putting the L.H.S. $= y$ (= a function of $[H^{\cdot}]$), for a minimum value of y (iso-electric point)

$$\frac{dy}{d[H^{\cdot}]} = 0$$

i.e. y is minimum when

$$-\frac{K_a[ROH]}{[H^{\cdot}]^2} + \frac{K_b[ROH]}{K_w} = 0$$

or when

$$[H^{\cdot}] = \sqrt{\frac{K_a.K_w}{K_b}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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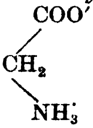
[1] More correctly in aqueous solution glycine forms zwitterions (internally neutralized), e.g.



from which the *p*H-value can be calculated, i.e. under this condition of *p*H the isoelectric point is reached. If the ampholyte is polyacidic and polybasic and can ionize as an acid and as a base in a variety of ways, and if the Law of Mass-Action holds for the different dissociations, and if it is assumed that the different dissociations are without influence on each other then, if K_{a_1}, K_{a_2}, K_{a_3} . . . are the dissociation constants of the different acidic groups, and K_{b_1}, K_{b_2}, K_{b_3} . . . are the dissociation constants of the basic groups, it may be shown that for the isoelectric point

$$[H^{\bullet}] = \sqrt{\frac{\Sigma K_a}{\Sigma K_b} . K_w} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In practice, however, the values of K_{a_2}, K_{a_3} . . . and K_{b_2}, K_{b_3} . . . are often small compared with K_{a_1} and K_{b_1} respectively, so that the influence of these small dissociation constants on the final result may be relatively insignificant.

It will be observed that in both of the formulae (1) and (2) the value of $[H^{\bullet}]$ for the isoelectric point is independent of the concentrations of the ampholyte and also of added electrolytes. If, however, a solution of the pure ampholyte is made (i.e. uncontaminated with other electrolytes), the hydrogen-ion concentration of such a solution will not, in general, be identical with that of the isoelectric point. This is readily shown by referring once again to the simple case of glycine. Since the sum of the charges on the anions in the solution must equal the sum of the charges on the cations,

$$[H^{\bullet}] + [R^{\bullet}] = [OH'] + [RO']$$

or

$$[H^{\bullet}] + \frac{K_b[ROH]}{[OH']} = [OH'] + \frac{K_a[ROH]}{[H^{\bullet}]}$$

hence, since

$$[OH'] = \frac{K_w}{[H^{\bullet}]}$$

$$[H^{\bullet}] = \sqrt{\frac{K_w + K_a[ROH]}{1 + \frac{K_b}{K_w}[ROH]}} \quad . \quad . \quad . \quad (3)$$

Equation (3) shows that the hydrogen-ion concentration of a solution of a pure ampholyte is, in part, dependent on the actual concentration. The more concentrated the solution, the more nearly will its *p*H-value approach the isoelectric point.

In the terminology of Michaelis, if the total concentration of the ampholyte = [A], and the concentration of the undissociated portion = [U], and if the concentration of the ampholyte cations = $[A^{\bullet}]$ while the concentration of the ampholyte anions = [A′], then the ‘undissociated fraction’, ρ, is given by

$$\rho = \frac{[U]}{[A]} = \frac{[A] - [A^{\bullet}] - [A']}{[A]}$$

While the foregoing Equations (1) and (2) for $[H^{\bullet}]$ are not quantitatively applicable to colloids, they may be applied qualitatively to all colloidal ampholytes. It has been mentioned that at the isoelectric point the sum of the anion and cation concentrations is minimum.

The isoelectric point would correspond to true chemical neutrality (pH = 7) only if $K_b = K_a$ (in the simpler case) or if $\Sigma K_b = \Sigma K_a$ (in the more complex case). In the case of proteins $\Sigma K_a > \Sigma K_b$ at the isoelectric point, hence the pH-value at the point in question < 7. At the isoelectric point the solubilities, stabilities, viscosities, and swelling (*q.v.*) of proteins are at their minima, and the phenomenon of electrophoresis is not displayed. Considerable variations are possible in the position of the isoelectric point of commercial gelatines. The position is influenced by the mode of preparation of the gelatine.[1] In theory, suspensoid sols should precipitate completely at their isoelectric points (electrophoretic mobility = 0), but in practice it has been found that they may precipitate over a range on either side of the points in question.

Hofmeister Series. Hofmeister, in 1888, proposed series arrangements of ions showing in descending order the effectiveness with which ions ' salt-out ' natural egg-albumin from its aqueous solution. The following was the series for anions : sulphate > orthophosphate > acetate > citrate > bicarbonate > chromate > chloride > nitrate > chlorate, there being a marked difference in the effectiveness between the initial members of the series and the final members.

For cations the order was as follows : lithium > sodium > potassium > ammonium > magnesium, the differences in this series not being as marked as in the case of anions.

It has since been found that such series show generally the order of effectiveness with which the ions mentioned are associated with a variety of phenomena in biology, ' crystalloid ' chemistry, and colloid chemistry. Pauli's order for cations in connexion with the ' salting-out ' of egg-albumin agreed with Hofmeister's, but for anions he gave : fluoride > sulphate > orthophosphate > citrate > tartrate > acetate > chloride > nitrate > chlorate > bromide > iodide > thiocyanate. It is interesting to note that when the solution was rendered acidic the orders were reversed.

' Hofmeister ' series (also known as ' lyotropic series ' and as ' specific ion effects ') have been tabulated to show, *inter alia*, the order in which anions of neutral salts affect the swelling and osmotic pressure of proteins (these effects being probably due to selective adsorption of ions), or the ' salting-in ' or peptizing of various substances, the order in which they assist in the reduction of the solubilities of gases in water, the order in which they assist in the ' salting-out ' of organic substances from solutions, and the order of hydration of the different ions. A marked degree of agreement is noted when the various published lists are compared, sometimes in the same sense (descending order of effectiveness), sometimes in opposite senses (some lists in descending order, others in ascending order).

For the precipitation of a silver sol Papada gave the following ionic series : aluminium > barium > strontium > calcium > hydrogen > caesium > rubidium > potassium > sodium > lithium.

Gold Number. Zsigmondy defined the ' gold number ' of a protective colloid as the number of milligrams of the protective colloid which just fails to prevent the change of colour of 10 ml. of a standard red gold hydrosol (containing from 0·0053 to 0·0058 per cent. of gold) to violet (indicative of aggregation) upon the addition of 1 ml. of a 10 per cent solution of sodium chloride. The gold number is an approximate measure of protective action (*q.v.*). The smaller the gold number, the greater the efficiency of the protective colloid. For this reason 'reciprocal gold numbers' are sometimes given to indicate directly the protective efficiency.

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[1] *See* Paper by Ames, *J. Soc. Chem. Ind.*, 1944, *63*, 200.

Rubin Number. The 'rubin number' is an alternative to the gold number as a measure of the protective efficiency of a hydrophilic colloid. According to Wo. Ostwald the rubin number is that mass, in grams, of the emulsoidal colloid per 100 ml. of solution which will just prevent the colour-change red ⟶ violet in a standard sol of the dye Congo-rubin[1] when 0·5 N potassium chloride is added under standard conditions. An 'iron number', involving the use of a ferric oxide sol, has also been suggested as an alternative.

Coehn's Rule. An empirical rule, due to Coehn, stated that when two substances are in contact, the one with the higher dielectric constant becomes positively charged, the one with the lower dielectric constant becoming negatively charged. Thus, the dielectric constant of glass is approximately 7, that of water being approximately 82, and that of turpentine approximately 2. In a suspension of glass in water the glass is negatively charged, whilst in a suspension of glass in turpentine the glass is positively charged. So many exceptions to the 'rule' are known that it is now considered to be of little merit.

Liminal (or Coagulating) Concentration (Liminal Value) (Coagulating Value). The 'liminal value' of a given coagulating electrolyte is the necessary and sufficient concentration of the electrolyte, in a mixture of a given hydrosol and the electrolyte, to effect complete precipitation of the sol. The numerical value of the liminal concentration largely depends on the valency and adsorbability of that ion of the electrolyte which is behaving as contra-ion. The liminal value is usually expressed in milligram-ions of contra-ion per litre, but it is sometimes given in milligram-equivalents of contra-ion per litre. Freundlich, for example, gave the liminal concentration of potassium nitrate for an arsenious sulphide sol (which sol is negatively charged) as 50. Suppose, therefore, it was required to coagulate 27 ml. of his arsenious sulphide sol with 3 ml. of a solution of potassium nitrate. The solution of potassium nitrate should originally have contained 500 milligram-ions of potassium per litre since, when mixed with the hydrosol, the final concentration of the potassium-ion in the mixture would have been only 50 milligram-ions per litre. (*See also* Coagulative Power under 'Precipitation'.)

Coacervation. Coacervation is the phenomenon of the separation into two immiscible liquid phases of a hydrophilic sol, the two liquid phases differing in the concentration of the dispersed phase, which phenomenon is sometimes observed, for example, on the addition of certain organic or inorganic liquids to the sol under certain conditions.

Gels and Gelation. The term 'gel' has been interpreted variously and some confusion has accordingly arisen in colloid literature. Ostwald used the term 'isogel' to describe any material (such as certain glasses in their transformation interval) in which the 'liquid' and 'solid' constituents are of similar chemical constitution although these constituents may differ in molecular weight. The term gel is commonly used to indicate the semi-solid transparent or opalescent jelly-like masses such as sometimes result from the cooling of sols (e.g. of 5 per cent gelatine or agar) or from partial evaporation of the dispersion medium. Such systems are capable of offering resistance to a finite shearing force. Strictly, gels consisting of substances with different molecular constitutions should be termed 'heterogels'. Graham used the term gel to describe any coagulum from a sol.

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[1] 'Congo-rubin' should not be confused with 'congo-red'.

If the original dispersion liquid was water, the gel is termed a 'hydrogel'. Freundlich suggested the term 'xerogel' for dried amorphous substances such as gelatine, gums, etc., which may be prepared by the removal of the fluid (e.g. by evaporation if the liquid be volatile) from a gel. This latter term arises through the fact that when the reduction in volume is substantially equal to the volume of the liquid removed (e.g. in the drying of a gelatine gel) the product, although harder and more rigid, often has an appearance similar to a gel. Weissenberger suggested that the term 'gel' be restricted to jellies, and that the discontinuous gelatinous coagula and precipitates (such as are usually obtained with the hydroxides of most of the metals) be termed 'coagels'. When the technique of fluid removal reduces shrinkage to a minimum and replaces the liquid by a gas, the resultant product is called an 'aerogel'. A gel such as that obtained by using bentonite clay is termed a 'suspensoidal gel'. Dry bentonite when placed under water swells with sorption (*q.v.*) of the liquid and reasonably uniform distribution of it throughout the mass, considerable swelling-pressure (*q.v.*) being developed in the initial stages. Especially when the particles are fine, the clay suspensions can possess the characteristic of a 'yield-point' and, even at very low concentrations, can set to jellies. Over large ranges of concentration they can exhibit plasticity in flow characteristics. When the proportion of water is too low, however, the mass may disintegrate on the application of a shearing stress. The yield-point of the suspension is often relatively uninfluenced by temperature-changes. A clay sol which can set to a gel has a 'time of setting' which is characteristic of the conditions. The rate of setting increases with increasing temperature (i.e. at higher temperatures the time of setting is less). Such gels, up to fairly high concentration-limits, when submitted to high shearing stresses break into smooth sols, but at very high concentrations they disintegrate (crumble) under the application of such stresses (*see* above).

A gel such as that obtained by using gelatine is sometimes termed an 'emulsoidal gel'. Gelatine swells spontaneously in water and initially exerts a high swelling-pressure. On warming to above 30° a sol is formed, which sol sets to a gel on cooling (*see* Preparations). Gelatine sols, up to high concentration limits, exhibit normal flow characteristics when above a certain temperature (or a narrow temperature range), with no indication of a yield value. Below this temperature (or temperature range) yield values are exhibited which increase rapidly with decreasing temperature. At higher temperatures gelatine sols will not set to gels, while at low temperatures the 'time of setting' decreases rapidly with decrease in temperature. Gelatine gels of high mechanical 'strength' (resulting from low temperature and/or high concentration) tend to disintegrate and rupture when high shearing stresses are applied.

A ‘ reversible ’ or ‘ heat-reversible ’ gel is one in which the gel-sol transformation may be repeated as often as desired by the correct choice of conditions, e.g. by temperature-change—gelatine and agar-agar gels are examples, but the gelation of gelatine may be rendered irreversible by the addition of formaldehyde. An ‘ irreversible ’ gel, once formed, cannot be reconverted into a sol by other than indirect methods—silicic acid gel is a common example.

Another kind of gel is known—the ‘ unstable ’ gel (e.g. of dibenzoyl-*l*-cystine) which, having formed from hot solution, segregates in the course of time into crystals and ‘ solvent ’.

Yet another kind of gel is such that it is formed by replacement of the solvent medium by a miscible ‘ non-solvent ’ liquid.

Some difficultly soluble salts which normally settle out as relatively large crystals can be obtained in such a manner that a ‘ jelly ’ or a gelatinous precipitate is formed. The condition in which such substances precipitate has, in particular, been studied by von Weimarn.[1] For simplicity in the treatment this author considers but two factors,[2] viz. (*a*) the solubility of the precipitating substance, (*b*) the concentration at which precipitation commences. The process of precipitation is divided into two stages, viz. stage (A) the condensation of molecules to invisible or ultramicroscopic nuclei or crystals, stage (B) the growth of these particles as a result of diffusion. For the first moments of stage (A) the equation is given :

$$W = K\frac{Q - L}{L} = K\frac{P}{L} = KU$$

where W = initial rate of precipitation ; Q = total concentration of the substance which is to precipitate ; L = solubility of coarse crystals of the substance ; P = amount of supersaturation = Q − L. $U = \frac{P}{L}$ = fractional supersaturation at the moment of inception of crystallization.

The velocity of the (B) stage is given by the Nernst-Noyes-Whitney equation :

$$V = \frac{D}{S}.A.(C - l)$$

where D = the diffusion coefficient ; A = the total area of the nuclei ; S = the length of the diffusion path as represented by the thickness of the adhering film ; C = the concentration of the surrounding solution ; l = the solubility of the dispersed phase for the given particle-size.

Von Weimarn concluded[3] that only high relative supersaturations can give a colloidal suspension or a gel, only concentrated solutions can give a gel, and only materials of low solubility can form stable gels or sols. Therefore for gel-formation the ratio $\frac{P}{L}$ must be very large (supersaturations, for example, of 204,500-fold). The nature of the precipitate, however, is influenced by the actual factor which makes $\frac{P}{L}$ large, for instance if it is large because of a high value of P, a gel is formed, whereas if it is large because of a low value of L, a sol results. Cases of gel-formation have been recorded, however, in which $\frac{P}{L}$ was relatively small.

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[1] Von Weimarn, *Grundzüge der Dispersoidchemie*, 1911, 30.

[2] The influence of a third factor (viscosity) is discussed in *Kolloidchem. Beiheft*, 1912, *4*, 101.

[3] For a criticism of von Weimarn's conclusions *see* Weiser, *The Colloidal Salts*, New York, 1928.

Von Weimarn called a gel formed by the use of substances such as barium sulphate a 'coarsely cellular gel', while gels formed by the use of substances such as gelatine he termed 'reticulated gels'. Gels resembling the gelatine variety are sometimes called 'elastic gels', whilst those resembling silicic acid gel are termed 'rigid gels'. Some gels (e.g. dilute bentonite gels) are converted (reversed) to sols when submitted to certain mechanical disturbances (e.g. gentle stirring, shaking, ultrasonic vibrations) only to be reconverted into gels on being re-allowed to stand. This phenomenon is called 'thixotropy', and such gels are called 'thixotropic gels'.

In the case of a bentonite suspension it has been shown [1] that the suspension may possess either of two different kinds of structure, (*a*) or (*b*). Structure (*a*) develops on continued regular stirring; structure (*b*) develops on the quiet standing of the system for a reasonable period. Structure (*b*) is characterized by a higher viscosity than structure (*a*), both types of structure having a viscosity greater than the suspension would have for zero time of standing or zero time of stirring after initial thorough mixing. The (*b*) kind of structure, if time is not allowed for its sufficient development, breaks down at a rapid rate if the system is stirred (much more rapid than the rate at which the (*a*) structure is developed by the stirring). Accordingly, in such a case, a minimum develops in the 'viscosity'–'time-of-stirring' curve. If the stirring of a bentonite suspension be effected in a MacMichael viscometer operating at a constant rate of rotation for a time, t, and if the value of the torque after the time in question be represented by T, and if the final steady value of the torque be denoted by T_∞, then it is found that

$$T = T_\infty + \frac{T_0'}{e^{kt}} + \frac{T_0 - T_\infty}{e^{kt}}$$

where T_0' and T_0 are factors the values of which vary according to the time of standing which elapses between the initial thorough mixing and the commencement of the stirring.

The ordinary sol-gel transformation usually appears to take place without evident discontinuities.[2] Gels appear to contain some sort of mechanical 'frame-work' (structure). This structure, however, would consist, in dilute systems, of a relatively small portion of the total mass of the system with a correspondingly small relative mechanical rigidity of the system. There is evidence that ordinary gels consist of thread-like or cell-like submicroscopic masses, formed by the partial coalescence of highly solvated hydrophilic constituent particles.

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[1] Broughton and Hand, *Am. Inst. Min. Met. Eng.*, Tech. Pub. No. 1002.

[2] *See*, however, Hatschek, *Kolloid-Z.*, 1929, *49*, 244.

Colloidal Magnitudes—Terminology. Particles visible in the ordinary microscope are often termed ' microns '. Particles of dimensions below the limit of ordinary microscopic vision are called ' ultramicrons '. If ultramicrons are ' visible ' using the ultramicroscope they are termed ' submicrons ' ; if they are not ' visible ' even with the aid of the ultramicroscope they are termed ' amicrons '. Amicrons would have ' diameters ' less than 10^{-7} cm., while submicrons would have ' diameters ' up to 200 $\mu\mu$.

Denaturation. ' Denaturation ' is a term frequently used in connexion with proteins. It denotes chemical changes, apparently[1] irreversible, which proteins in solution undergo as a result of the action of ultra-violet light, X-rays, heat, alcohol, acetone, adsorption in foam, &c.

The ' heat coagulation ' of proteins has been shown to take place in two stages, (*a*) denaturation, and (*b*) flocculation (if conditions are suitable). The mechanism of process (*a*) is not fully understood.

Syneresis. ' Syneresis ' is a phenomenon, displayed to a greater or less extent by all gels, in which the gel, on being placed in a glass vessel which is then corked to prevent evaporation (the vessel having been previously vaselined, if necessary, on the inside to prevent the adherence of the gel to the glass), begins to contract and to exude spontaneously some of the liquid phase (e.g. water or an aqueous solution).

Thixotropy. *See* under ' Gels and Gelation '.

Rheopexy. Although the gel-sol transformation in thixotropic gels is occasioned by mechanical disturbance, the rate of re-setting of the gels (the sol-gel transformation) on standing may, in some cases, be increased by certain types of mechanical disturbance (e.g. vibration caused by tapping). This anomalous phenomenon is termed ' rheopexy '.

Ampholyte. The term ' ampholyte ' is a contracted form of the term ' amphoteric electrolyte '.

Colloidal Electrolytes. A colloidal electrolyte is a salt (e.g. sodium palmitate) in which, when dissolved, numbers of the ions of one kind (e.g. of palmitate ions) are replaced by ionic micelles. In addition to the alkali salts of higher organic acids mention may be made of certain dyestuffs (e.g. the Congo group), clays, higher sulphonic acids (e.g. cetyl sulphonic acid), gelatine salts, gum agar, &c.

Micellar Weight. The ' micellar weight ' is the mass of a micelle on the scale O = 16. The term ' molecular weight ' (of a micelle) is sometimes used, the micelle being regarded as a giant molecule. One method of determining micellar weights, applied to protein sols, depends on the equilibrium which is finally established between the rate of diffusion of the particles and their rate of sedimentation under the influence of an applied centrifugal force (Sedimentation Equilibrium Method).

If a sol be centrifuged in a closed cell, the force influencing the sedimentation of a dispersed particle is given by

$$F_1 = \frac{4}{3}\pi a^3(d_1 - d_2)\omega^2 x \quad . \quad . \quad . \quad . \quad (4)$$

where *a* is the radius of the particle (assumed uncharged and spherical) ;

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[1] The irreversibility is merely apparent. *See*, for example, Anson and Mirsky, *J. Phys. Chem.*, 1931, *35*, 185.

d_1 is the density of the particle-material as it exists in the sol-system ; d_2 is the density of the dispersion medium ; ω is the angular velocity of the particle about the axis of the centrifuge ; x is the radius of the circle described by the particle about the axis of the centrifuge.

Equation (4) may also be written

$$F_1 = \frac{4}{3}\pi a^3\left(\frac{d_1}{d_1} - \frac{d_2}{d_1}\right)\omega^2 x = m\left(1 - \frac{d_2}{d_1}\right)\omega^2 x = m(1 - Vd_2)\omega^2 x \quad . \quad (5)$$

where m is the mass of a single particle ; V is the partial specific volume of the particle. In practice, the value of V may be determined by means of the pyknometer, as follows :

Let w_1 grams of the sol system fill the pyknometer, and suppose this contains w_2 grams of the dispersed substance. It therefore contains $(w_1 - w_2)$ grams of the solvent. Let w grams of the pure solvent fill the pyknometer.

Then, since the density of the pure solvent is d_2 grams per ml., the capacity of the pyknometer is $\frac{w}{d_2}$ ml. When the pyknometer is filled with the sol system, the $(w_1 - w_2)$ grams of the solvent in the system occupies a partial volume of $\frac{w_1 - w_2}{d_2}$ ml.

Hence w_2 grams of the dispersed substance occupies a partial volume of $\left\{\frac{w}{d_2} - \frac{w_1 - w_2}{d_2}\right\}$ ml., or the partial volume occupied by 1 gram of the dispersed substance (i.e. the partial specific volume) $= \frac{w - (w_1 - w_2)}{w_2 d_2}$ ml.

When the limiting velocity, v_1, of sedimentation is reached, the frictional force per particle, F_2, opposing the motion is, according to Stokes' Law (since the particle is large compared with ordinary molecular dimensions) given by

$$F_2 = 6\pi\eta a v_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where η is the coefficient of viscosity of the liquid. Since no acceleration is being produced in this limiting condition, it follows that

$$F_2 = F_1$$

or

$$6\pi\eta a v_1 = m(1 - Vd_2)\omega^2 x$$

therefore the limiting velocity, (v_1), is given by

$$v_1 = \frac{m(1 - Vd_2)\omega^2 x}{6\pi\eta a} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Assume that the sol has a concentration C moles (gram-micelles) of solute per ml. Then under the steady velocity v_1, the number of moles of solute transported per second through a cross-sectional area, which is perpendicular to the direction of the sedimentation, of 1 sq. cm. would be equal to v_1C, i.e. from (7), would be equal to

$$\frac{Cm(1 - Vd_2)\omega^2 x}{6\pi\eta a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Opposed to the phenomenon of sedimentation is the phenomenon of diffusion, i.e. when the sol has been centrifuged for a sufficiently long time an equilibrium is reached when sedimentation and diffusion balance each other. If we choose the direction of the radius x as a reference x-axis for the direction of the diffusion, and if $\frac{dC}{dx}$ is the rate of change of the concentration C, in moles per ml., of the diffusing material along the axis x, then the quantity in moles of the solute transported through the cross-sectional area of 1 sq. cm., towards the axis of the centrifuge, may be given as $D\frac{dC}{dx}$, where D is a coefficient (called the Diffusion Constant or Diffusion Coefficient).

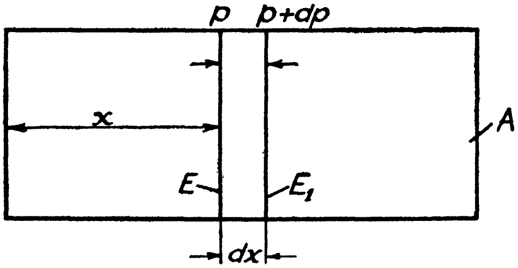

FIG. 10 (XV³)
Cylindrical vessel with axis in direction of x

To calculate the value of D: In Fig. 10 (XV³), let A represent a cylindrical vessel of cross-section 1 sq. cm., with its axis in the same direction as x. Let p and $(p + dp)$ respectively be the osmotic pressures at the planes E and E_1 which are a distance dx apart. Then dp is the osmotic force acting on the material dissolved in the $(dx \times 1)$ ml., or $\frac{dp}{dx}$ = osmotic force acting on the material dissolved in 1 ml. If it be assumed that the osmotic pressure follows the ordinary law for dissolved substances in dilute solution then,

$$p = \mathrm{CRT}$$

or

$$\frac{dp}{dx} = \mathrm{RT}\frac{dC}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now there are NC particles of the dispersed substance in 1 ml. (where N = Avogadro's Number), hence the osmotic force acting on a single particle of the dissolved material

$$= \frac{\mathrm{RT}}{\mathrm{NC}} \cdot \frac{dC}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Again invoking Stokes' Law, the frictional force per particle at the limiting velocity, v_2, is given by the expression $6\pi\eta a v_2$. Since there is equilibrium between the osmotic force and the frictional force when the velocity of diffusion is steady,

$$6\pi\eta a v_2 = \frac{\mathrm{RT}}{\mathrm{NC}} \cdot \frac{dC}{dx}$$

or

$$v_2 = \frac{\mathrm{RT}}{6\pi\eta a \mathrm{NC}} \cdot \frac{dC}{dx} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Also since the quantity, in moles, of the solute transported per second, through a cross-sectional area of 1 sq. cm., as a result of the diffusion process, is given by the expression v_2C, this quantity may, from (11), be written $\frac{RT}{6\pi\eta a N}\cdot\frac{dC}{dx}$. But this quantity has already been denoted by D$\frac{dC}{dx}$, wherefore

$$D = \frac{RT}{6\pi\eta a N} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Now in the process of the centrifuging of a protein sol an equilibrium is finally established between the rate at which particles tend to move in the direction of the periphery due to centrifugal force, and the rate at which they tend to move in the opposite direction (towards the axis of rotation) due to diffusion. For this equilibrium, v_1 and v_2 may be equated, hence from (7) and (11),

$$\frac{m(1 - Vd_2)\omega^2 x}{6\pi\eta a} = \frac{RT}{6\pi\eta a NC}\cdot\frac{dC}{dx}$$

wherefore

$$Nm = \frac{RT}{(1 - Vd_2)\omega^2 xC}\cdot\frac{dC}{dx}$$

But Nm = M (where M grams is the gram-molecular (gram-micellar) weight of the particles), hence on integrating between the limits x_1 and x_2, C_1 and C_2, the molecular weight, M, is given by the equation

$$M = \frac{2RT \log_e \frac{C_2}{C_1}}{\omega^2(1 - Vd_2)(x_2{}^2 - x_1{}^2)} \quad . \quad . \quad . \quad . \quad (13)$$

Since the Stokes' Law ' terms ' are eliminated in Equation (13), this equation does not involve a term for the shape of the particles. Accordingly its validity is independent of particle-shape, although the equation holds for dilute solutions only and has to be modified when the solute is electrolytically dissociated.

Another method of micellar weight determination is based on actual rate of sedimentation. After a short initial period of centrifuging, the molar centrifugal force (centrifugal force per mole) = M(1 − Vd_2)$\omega^2 x$. This becomes equal to the opposing molar frictional force, $f\left(\frac{dx}{dt}\right)$, where f = the molar frictional coefficient.

If it be assumed that $f = 6\pi\eta a N$,

then

$$M = \frac{6\pi\eta a N}{(1 - Vd_2)\omega^2 x}\cdot\frac{dx}{dt}$$

or

$$M = \frac{RT}{D(1 - Vd_2)\omega^2 x}\cdot\frac{dx}{dt} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Integrating between the limits x_1 and x_2, t_1 and t_2,

$$M = \frac{RT \log_e \frac{x_2}{x_1}}{D(1 - Vd_2)\omega^2(t_2 - t_1)} \quad . \quad . \quad . \quad . \quad (15)$$

For small intervals of x, (14) may be written

$$M = \frac{RTS}{D(1 - Vd_2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where $S = \frac{1}{\omega^2 x} \cdot \frac{dx}{dt}$. S is called by The. Svedberg the 'sedimentation velocity constant' as it is constant for a given species of micelle in a given solvent at a given temperature.

Alternative Method of evaluating the Diffusion Constant ('Problem of the 'Irregular Path'). In Fig. 11 (XV³), let A again be a cylindrical vessel of cross-section 1 sq. cm., with its axis parallel to the axis of x, containing a sol so dilute that there is little interaction between the dispersed particles themselves. Each particle (assumed spherical), however, is subjected to a series of haphazard molecular impacts, so that the particle traces out an irregular path—Brownian movement.

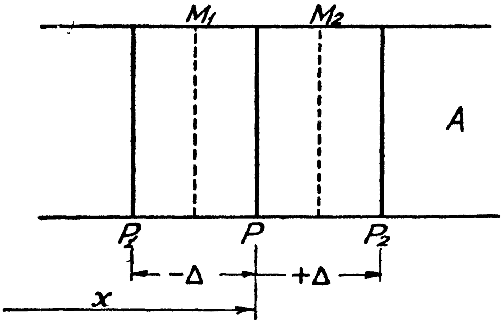

FIG. 11 (XV³)
Cylindrical vessel with axis parallel to x

Consider the particles at the plane P at a certain instant. In a short interval of time, t, after this instant (so short that concentrations have not varied appreciably), the particles in question will have covered the various distances, measured parallel to the x-axis, of Δ_1, Δ_2, Δ_3 . . . some in the positive direction, others in the negative direction.

Assume the average distance (positive or negative) covered by each particle in the time t to be Δ, half of the particles covering $+\Delta$, and the other half $-\Delta$. These particles which, in the time-interval, t, pass through the plane P must, at the commencement of this interval, have been distant from P by an average amount not greater than $\pm\Delta$, i.e. they must have been present in the space between the planes P_1 and P_2. Suppose the average concentration in the space P_1P, i.e. the concentration at the mean plane M_1, to be C_1 moles per ml. Then since half the particles move to the right, the number of moles passing through P from the space P_1P in the time $t = \frac{1}{2}C_1\Delta$.

Also, if the average concentration in the space PP_2 (concentration at the mean plane M_2) $= C_2$ moles per ml., the number of moles passing through P from the space PP_2 in the time $t = \frac{1}{2}C_2\Delta$. On the whole, therefore, the net diffusion towards the left through P in the time $t = \frac{1}{2}(C_2 - C_1)\Delta$ moles per sq. cm. If the co-ordinate of the plane P is x, then

$$\frac{dC}{dx} = \frac{C_2 - C_1}{\Delta}$$

$$\therefore \tfrac{1}{2}\Delta^2 . \frac{dC}{dx} = \tfrac{1}{2}(C_2 - C_1)\Delta$$

Hence, $\frac{1}{2}\Delta^2\frac{dC}{dx}$ moles diffuse through 1 sq. cm. in the time t, or, $\frac{1}{2t}\Delta^2\frac{dC}{dx}$ moles diffuse through 1 sq. cm. in 1 second. But this latter quantity has already been written $D\frac{dC}{dx}$. Accordingly,

$$D = \frac{1}{2t}\Delta^2 \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The term $\frac{\Delta^2}{t}$ is called the 'activity' of the particle. Einstein[1] equated the values of D shown in (17) and (12), viz.

$$\frac{1}{2t}\Delta^2 = \frac{RT}{6\pi\eta a N}$$

whence

$$\Delta = \sqrt{\frac{tRT}{3\pi\eta a N}} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Equation (18) therefore gives the average displacement[2] in a time t along the x-axis, due to Brownian movement, of a spherical particle of radius a in a liquid with a coefficient of viscosity η. Accordingly, for a given particle in a given liquid at a steady temperature, $\Delta \propto \sqrt{t}$.

Rotational Brownian Movement. The particles in a suspension are also subject to rotational motion. The Einstein equation for the R.M.S. angle of rotation, α, in a time, t, relative to an arbitrary axis is:

$$\alpha = \sqrt{\frac{tRT}{4\pi N\eta a^3}}$$

The Perrin Distribution Law. Perrin showed that the law of distribution of particles in a colloidal suspension is analogous to, and is an accentuated form of, the law which governs the distribution of molecules in (still) atmospheric air. The assumption is made, as formerly indicated, that the colloidal particle is a giant molecule (uncharged) so that its mean kinetic energy, in a state of equilibrium of the sol, may be considered as equal to the mean kinetic energy of a molecule of the dispersion

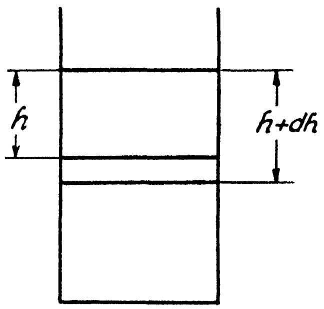

FIG. 12 (XV^8)
Vertical vessel of cross-section area S

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[1] *Z. Elektrochem.*, 1908, *14*, 235. *See* also Drude's *Ann.*, 1905, *17*, 549; and *ibid.*, 1906, *19*, 289, 371.

[2] In fact, Δ is the R.M.S. displacement.

medium. Let Fig. 12 (XV[3]) represent a quantity of a suspension of uniform particles in equilibrium in a vertical cylinder of cross-sectional area S. Consider a section of the suspension bounded between horizontal planes at depths h and $(h + dh)$. The condition of equilibrium would not be disturbed if two semi-permeable pistons (permeable to the solvent only) were placed at the planes in question. Let the concentration of the suspension be C moles per ml. at the depth h, and $(C + dC)$ moles per ml. at the depth $(h + dh)$. Then assuming the ordinary osmotic pressure equation, the osmotic pressure at the depth h will be CRT, and at the depth $(h + dh)$ will be $(C + dC)$ RT.

The net osmotic pressure acting will therefore be $RTdC$, hence the net osmotic force will be

$$SRTdC \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The total apparent weight of the particles in the section will be

$$NCV(d_1 - d_2)gSdh \quad . \quad . \quad . \quad . \quad (20)$$

where V is the volume of one of the particles, the remaining symbols having the same significance as previously. Since there is an equilibrium established within the section, the opposing forces (19) and (20) must balance, hence

$$\frac{dC}{C} = \frac{NV(d_1 - d_2)gdh}{RT}$$

Integrating between the limits C_0 and C_1, h_0 and h_1,

$$\log_e \frac{C_1}{C_0} = \frac{NV(d_1 - d_2)g(h_1 - h_0)}{RT}$$

or, if the concentrations C_1, C_0 correspond to numbers of particles n_1, n_0 respectively per ml., then

$$\log_e \frac{n_1}{n_0} = \frac{N}{RT} . V(d_1 - d_2)g(h_1 - h_0) \quad . \quad . \quad . \quad (21)$$

Equation (21) shows that in a suspension of uniform particles in equilibrium at a uniform temperature, the concentration of the particles should increase in an exponential manner as a function of the increasing depth, i.e. as the depths increase in arithmetical progression, the concentrations should increase in geometrical progression. Perrin verified this law experimentally for depths up to 0·1 mm. Some of his observed and calculated values of n for different depths in a suspension of substantially uniform gamboge [1] particles after equilibrium had been reached are indicated in the following table:

TABLE II

Depth (h) in μ	n (observed)	n (calculated from Equation (21))
0	100	—
25	116	119
50	146	142
75	170	169
100 (= 0·1 mm.)	200	201

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[1] Gamboge is a gum-resin from the *Stalagmites cambogiodes* tree and allied species grown in Ceylon and Siam.

By determining V (from the particle-diameter), d_1, d_2, and substituting the values of R, T, g, Perrin was able to evaluate Avogadro's Number, N, from a large number of results similar to those shown in Table II.

Doubt has been expressed [1] whether the law of Equation (21) holds for depths much greater than 0·1 mm. (e.g. of the order some millimetres), although Westgren [2] obtained good agreement in the case of gold sols over a total depth of 1 mm.

Influence of Electrical Charges on the Perrin Equilibrium. In deriving Equation (21), no attention was paid to the repulsion caused by the like electrical charges on the particles themselves. Consider a layer dh of the suspension. The net electrical force acting on the particles in the layer dh may be of the form knq per unit electrostatic charge in the layer dh, where q is the charge on each particle, n is again the number of particles per ml., and k may be, in the regions near the surface, regarded as a constant.

Since there are $qnSdh$ units of charge in the layer dh, the total net force acting on the particles in this layer, due to electrical effects, would be $(knq)\,(qnSdh)$, i.e. kq^2n^2Sdh, which net force may be considered to be the excess of upward repulsion (due to particles below dh) over that of downward repulsion (due to particles above dh).

Since this repulsion acts against the force of gravity, the equation already obtained by equating (19) and (20), may be modified to

$$SRTdC = NCV(d_1 - d_2)gSdh - kq^2n^2Sdh$$

or

$$\frac{RT}{N}.dn = nV(d_1 - d_2)gdh - kq^2n^2dh$$

This equation may be written

$$K_1dn = (K_2n - K_3n^2)dh \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where

$$K_1 = \frac{RT}{N}\,; \quad K_2 = V(d_1 - d_2)g\,; \quad K_3 = kq^2$$

From Equation (22)

$$n = \frac{K_3}{K_2 + K_4e^{-\frac{K_3}{K_1}h}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where

$$K_4 = \frac{K_3 - K_2n_0}{n_0}$$

n_0 being the value of n at the surface.

If, in Equation (23), the term $\frac{K_3}{K_1}h$ is large, n becomes substantially equal to $\frac{K_3}{K_2}$, a constant. In practice, the value of $\frac{K_3}{K_1}h$ usually becomes large at a short distance below the surface, and then the value of $n\left(= \frac{K_3}{K_2}\right)$ remains steady.

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[1] *See* Burton, *Proc. Roy. Soc. A.*, *100*, 705; Porter and Hedges, *Trans. Farad. Soc.*, 1922, *18*, 1.

[2] *Z. physik. Chem.*, 1915, *89*, 63.

Near the surface, where n varies with depth, as the value of h approaches zero, the value of $e^{-\frac{K_3}{K_1}h}$ approaches unity, therefore at such a position $n_0 \doteqdot \frac{K_3}{K_2 + K_4}$. It is held that K_4 may be large when compared with K_2. Accordingly,

$$n_0 \doteqdot \frac{K_3}{K_4}, \text{ or } K_4 \doteqdot \frac{K_3}{n_0}$$

The value of n therefore, in the case where h is small, may be written

$$n = \frac{K_3}{K_4 e^{-\frac{K_3}{K_1}h}}$$

or,

$$n = n_0 e^{\frac{K_3}{K_1}h}$$

Functions of Dispersion. By the term 'functions of dispersion' is meant the variations of properties (chemical or physical) in relation to the degree of dispersion (*see* under). Thus if the surface tension, rate of sedimentation, viscosity, &c., of a particular kind of sol system be determined for different particle-sizes, the functions of dispersion of the material constituting the dispersed phase are obtained.

Degree of Dispersion. The 'degree of dispersion' means the relative fineness of the particles of the dispersed phase. According to von Weimarn, if G_m = mean size of precipitate crystals as measured in gram-molecules, then $D_m = \frac{1}{G_m}$ = the degree of disintegration (or degree of dispersity) of the precipitate. According to Kick's Law the energy, E, required to crush a material from an original linear dimension L_0 to a final linear dimension L_f is given by the equation

$$E = k \log_e \frac{L_0}{L_f}$$

where k is a constant for the given material, whereas according to Rittinger's Law the energy, E, necessary to crush a cube of length D units to cubes of length d units is given by

$$E = 3AD^3\left(\frac{1}{d} - \frac{1}{D}\right)$$

where A is a coefficient.

Sorption. 'Sorption' is a general term, introduced by McBain, which covers the phenomena of 'adsorption' and 'absorption'. The corresponding verb is 'sorb.'

Electro-viscous Effect. If neutral electrolytes be added to an emulsoid sol in concentrations which would be sufficient to flocculate a suspensoid sol (e.g. in milli-equivalents), although no flocculation occurs the particles lose their charge. This loss of charge is made evident, for instance, by the relatively large diminution in the viscosity of the system due to the disappearance of the 'electro-viscous effect.' The electro-viscous effect is the phenomenon of the increase of the viscosity of the sol due to the charge.

The quantity of electrolyte needed to remove the electro-viscous effect depends on the valency of the ion the charge of which is opposite in sign to that of the particle. The electro-viscous effect has also been termed the ‘ quasi-viscous effect ’.

The diminution in viscosity has been attributed to a decrease in the total effective volume of the particles of the dispersed phase. This decrease may be due to either or both of two circumstances (*a*) shrinkage of the individual dispersed particles, (*b*) clumping of the particles. de Jong and Gwan [1] found that 1 milli-equivalent of electrolyte caused a pronounced decrease in the viscosity of a sol, the valency of the cation being of importance.

Smoluchowski's modification of the Einstein viscosity-equation was (*cf.* p. 398) as follows:

$$\frac{\eta_1 - \eta}{\eta} = \frac{5}{2}\varphi\left[1 + \frac{1}{\kappa\eta r^2}.\left(\frac{\zeta D}{2\pi}\right)^2\right]$$

where κ = the specific conductance ; r = radius of the particle ; D = dielectric constant ; ζ = zeta-potential of the double-layer.

Tyndall Effect. If a beam of light be passed through a fluid containing dispersed particles, the path of the light, when viewed at right angles to the direction of propagation, may become clearly marked. This phenomenon, which is well illustrated in the passage of a beam of light from a projection lantern through air containing tobacco-smoke or dust, is termed the ‘ Tyndall effect ’. If the particles are dispersed as in an ordinary solution the phenomenon is not observed.[2] If a beam of light be brought to a focus in a colloidal solution a bright cone (a ‘ Tyndall cone ’) is obtained.

Solid-phase Rule (Disperse-phase Rule) (‘ Bodenkorperregel ’).[3] This rule states that peptizability or colloidal solubility of a substance is not independent of the quantity of solute present. The concentration of the dispersed substance in the sol may increase continuously with the quantity of the solute substance present in the system, or it may show a maximum value for an intermediate amount of the solute. Analogously, if a sol be partially coagulated, and if a portion of the coagulum be removed from the system, and if what remains of the system be shaken, the concentration of the dispersed constituent will change, either increasing or decreasing according to circumstances. These phenomena offer a marked contrast to the ‘ solubility laws ’ of classical physical chemistry, viz. that for a given solute and solvent the equilibrium is attainable from both sides (undersaturation and supersaturation) and that the ‘ true ’ solubility depends only on the temperature and (to a less extent) on the pressure, being practically independent of particle-size in the case of particles larger than a particular critical size.

Ultrafiltrate. The term ‘ ultrafiltrate ’ denotes a filtrate obtained as a result of the process of ultrafiltration (*q.v*).

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[1] *Kolloidchem. Beihefte.*, 1929, *29*, 436.

[2] This is not absolutely true. There is also, in the case of true solutions, a very weak scattering of light. In this case the wavelength of some of the scattered light is changed in a manner which depends on the nature of the molecules which scatter it (Raman Effect).

[3] *See*, for instance, Wo. Ostwald and von Buzágh, *Kolloid-Z.*, 1927, *41*, 163, 169 ; *ibid.*, 1927, *43*, 215, 220 ; *ibid.*, 1929, *48*, 33 ; *ibid.*, 1930, *50*, 65.

Swelling. When a piece of 'leaf' gelatine is placed in cold water it imbibes the water to such an extent that the leaf swells considerably. In a similar manner rubber swells in benzene. Again, high-level polymers of styrene (polystyrenes) will swell in contact with benzene. These are illustrations of the phenomenon of 'swelling', a phenomenon exhibited by certain xerogels when they are placed in liquids (or their vapours)[1] for which they have an affinity. The process of swelling is commonly an exothermic one, and is accompanied by small but important amounts of shrinkage in *total* volume. In the initial stages of the swelling considerable 'swelling pressures' may be developed—this could be shown by opposing the swelling by a membrane permeable to the solvent but not to the solute. 'Limited swelling' is said to take place if a gel of definite volume is finally formed when a given mass of the material swells without hindrance in excess of the 'solvent' liquid. When, however, the swelling proceeds to such an extent that a sol is ultimately formed, the swelling is described as 'unlimited'.

There is much resemblance between the phenomenon of swelling and that of osmosis in sols. If the process of swelling be regarded as a reversible one, an expression for the value of the swelling pressure may be developed thermodynamically as follows:

Suppose that *dm* gram of the solvent be removed isothermally and reversibly from the partly swollen material by evaporation at the vapour pressure, P_w, of the solvent-vapour over this swollen material followed by compression (out of contact with the material) of the vapour thus removed to a pressure P_0 (the saturation vapour-pressure of the pure solvent at the temperature chosen), and then by condensation to liquid at the pressure P_0.

If the vapours follow the gas laws, the net work done will be

$$dA = \frac{RTdm}{M} \log_e \frac{P_o}{P_w} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where M = molecular weight of the vapour. Assuming that the removal of the *dm* gram of liquid solvent might also be accomplished isothermally and reversibly by means of a suitable membrane, the work done in such a removal would be

$$dA = \frac{P}{\rho} . dm \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where P = swelling pressure; ρ = density of the liquid. Neglecting any slight difference between the volume of liquid removed $\left(\frac{dm}{\rho}\right)$ and the reduction in volume of the swollen material (dv), (25) may be written

$$dA = Pdv \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Combining (24) and (26), $Pdv = \frac{RT}{M} . dv . \log_e \frac{P_0}{P_w}$

or P (the swelling pressure) $= \frac{RT}{M} \log_e \frac{P_0}{P_w}$.

Since the process of swelling is an exothermic one, it is favoured at lower temperatures. The amount of over-all contraction experienced when swelling takes place is relatively greatest in the initial stages of the process.

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[1] *See* under 'The Schröder Paradox'.

Swelling is affected by the presence of added substances both of electrolyte and non-electrolyte character. The effect of electrolytes, however, is not identical with the effect which these substances exert on the building of gel structure. In gel-formation, electrolytes may accelerate or retard the process according to the natures of the ions present and according to which of the ions is preferentially adsorbed. In the process of swelling, the effect of electrolytes is connected with dispersion phenomena and is also usually held to be connected with the establishment of a Donnan equilibrium (although this may actually be related to the phenomenon of adsorption).

The Donnan [1] Equilibrium. If an aqueous solution, I, of an electrolyte, $Na\bar{R}$, is separated from an aqueous solution II, of sodium chloride by means of a membrane which is permeable to all the ions except $\bar{R}'$, then Na-ions cannot pass through the membrane from I to II on account of the electrostatic attraction of the $\bar{R}$-ions which are themselves unable to pass through the membrane. It is possible, however, for the Na-ions and for the Cl-ions to pass from solution II to solution I (since the membrane is permeable to both of these ions), and such a process occurs in practice until a certain distribution of ions is reached. The final concentrations of the different ions on both sides of the membrane is calculable from the initial concentrations, as indicated in the following:

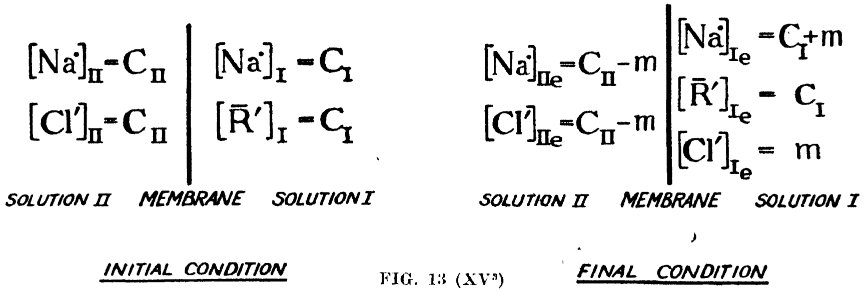

FIG. 13 (XV³)
The Donnan equilibrium

Let the initial condition and the final condition be represented [2] as in Fig. 13 (XV³). At the final ('equilibrium') condition, let δn gram-ion of $Na^{\cdot}$ and of Cl' be transferred isothermally, reversibly, and at constant volume from solution II to solution I. Since, under the conditions chosen, no work is done, then

$$\delta n \mathrm{RT} \log_e \frac{(\mathrm{C_{II}} - m)}{(\mathrm{C_I} + m)} + \delta n \, \mathrm{RT} \log_e \frac{(\mathrm{C_{II}} - m)}{m} = 0$$

or,

$$\frac{(\mathrm{C_{II}} - m)}{(\mathrm{C_I} + m)} = \frac{m}{(\mathrm{C_{II}} - m)}$$

i.e.

$$(\mathrm{C_{II}} - m)(\mathrm{C_{II}} - m) = (\mathrm{C_I} + m)(m) \quad . \quad . \quad . \quad (27)$$

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[1] *See*, for example, Donnan, *Z. Elektrochem.*, 1911, *17*, 572; *Chem. Rev.*, 1924, *1*, 73; *Kolloid-Z.*, 1932, *61*, 160. Also Hückel, *Kolloid-Z.*, 1925, *36*, 204; Donnan, 'Colloidal Electrolytes', *Trans. Farad. Soc.*, 1935, *31*, 80.

[2] The suffix *e* denotes the equilibrium condition.

or, when ‘ equilibrium ’ sets in, the product of the concentrations of the pair of oppositely charged diffusible ions on one side of the membrane is equal to the product of the concentrations of the same pair of ions on the other side.

In the particular case quoted, the result may be written

$$[\mathrm{Na}^{\cdot}]_{\mathrm{II}e} \times [\mathrm{Cl}']_{\mathrm{II}e} = [\mathrm{Na}^{\cdot}]_{\mathrm{I}e} \times [\mathrm{Cl}']_{\mathrm{I}e}$$

In general, if the salt with the two diffusible ions is represented by $\mathrm{K}_{\beta}\,\mathrm{A}_{\alpha}$ (the metallic ion, K, being α-valent, and the acidic ion, A, being β-valent), and if the other electrolyte contains the metallic radicle K as the single ‘ diffusible ’ ion, then

$$[\text{K-ions}]^{\beta}_{\mathrm{II}e} \times [\text{A-ions}]^{\alpha}_{\mathrm{II}e} = [\text{K-ions}]^{\beta}_{\mathrm{I}e} \times [\text{A-ions}]^{\alpha}_{\mathrm{I}e}$$

If, in the simpler case, $\mathrm{C}_{\mathrm{II}} - m = x$, $m = y$, and $\mathrm{C}_{\mathrm{I}} = z$, then $\mathrm{C}_{\mathrm{I}} + m = y + z$, and the equilibrium condition (27) may be written

$$x^2 = (y + z)y,$$

or

$$x = y\sqrt{1 + \frac{z}{y}}$$

and since z and y are both positive,

$$x > y \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Also $\qquad (x) + (x) < (y + z) + (y)$

or $\qquad 2x < 2y + z$

wherefore $\qquad x < y + \tfrac{1}{2} z$

and, *a fortiori*,

$$y + z > x \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Accordingly, from (28) and (29),

$$[\mathrm{Cl}']_{\mathrm{II}e} > [\mathrm{Cl}']_{\mathrm{I}e}, \text{ and } [\mathrm{Na}^{\cdot}]_{\mathrm{I}e} > [\mathrm{Na}^{\cdot}]_{\mathrm{II}e}$$

Consequently a difference of electric potential will be established between I and II.

By equating (*a*) the electrical work done when $\delta n\mathrm{F}$ coulombs of positive electricity are transported, at equilibrium, isothermally and reversibly, from solution II to solution I, and (*b*) the osmotic work done in transferring $\tau\delta n$ gram-ion of $\mathrm{Na}^{\cdot}$ from solution II to solution I and $(1 - \tau)\delta n$ gram-ion of Cl' from solution I to solution II (where τ and $(1 - \tau)$ are the transport numbers of $\mathrm{Na}^{\cdot}$ and Cl' respectively), it may be shown that the difference of potential, E, between the two sides of the membrane is given by

$$\mathrm{E} = \frac{\mathrm{RT}}{\mathrm{F}} \log_e \frac{x}{y}$$

or, in general, when the ions concerned in the equilibrium have each the valency of v,

$$\mathrm{E} = \frac{\mathrm{RT}}{v\mathrm{F}} \log_e \frac{x}{y}$$

where F = 96,540 coulombs, and R, T have the customary significance.

In the Proctor-Wilson theory[1] of swelling it is held that gelatine is an elastic gel insoluble in water but completely permeable to that liquid, and that the gelatine is capable of forming definite compounds with acids, e.g. gelatine hydrochloride with hydrochloric acid. Such a compound (gelatine hydrochloride) is taken to be soluble in water and, in aqueous solution, to be completely dissociated. Whereas the gelatine-ion cannot diffuse through the surface of the gel, chloride-ion can. The gelatine therefore behaves as a ' semi-permeable ' membrane. In the swelling of gelatine in acids, most of the hydrogen-ion of the interdiffusing acid combines with the gelatine which, accordingly, is converted into positively charged micelles, the balancing negative charges being provided by anions from the acid. The intermicellar liquid contains acid-anions and some free hydrogen-ions, and the outer acidic liquid contains both of these kinds of ions. When a Donnan equilibrium is attained, assuming the acid to be hydrochloric, the following holds

$$[\mathrm{H}^{\bullet}]_{\varepsilon_e} \times [\mathrm{Cl}']_{\varepsilon_e} = [\mathrm{H}^{\bullet}]_{i_e} \times [\mathrm{Cl}']_{i_e}$$

where the symbol ε refers to the external acidic solution and the symbol i refers to the interior of the ' gel-phase '.

If (as before) at equilibrium, x = concentration of hydrogen-ion in the external acidic solution = concentration of chloride-ion in the external acidic solution, y = concentration of free hydrogen-ion in the interior of the gel-phase, and z = concentration, in the interior, of those chloride-ions which balance the positively charged gelatine-micelles, then the total concentration of chloride-ion in the intermicellar liquid $= y + z$. As before, $(y + z) + (y) > (x) + (x)$.

Let $2y + z - 2x = \mathrm{C}$. Then C represents the excess of the concentration of diffusible ions in the gel-phase over their total concentration in the external acidic solution. It is because of this excess that water diffuses by osmosis into the pores and capillary spaces of the gel to cause swelling. This swelling continues until the diffusing-force is just balanced by the cohesive-forces of the gel-structure. The swelling is proportional to C, and the maximum swelling should occur at the same hydrogen-ion concentration as that which causes maximum osmotic pressure.[2]

Wilson further applied Hooke's Law to the phenomenon, and put

$$\mathrm{C} = k\mathrm{V},$$

where k was a factor which resembled the bulk-modulus of elasticity of the gelatine, and V was the increase in the volume of the gel. Mardless has found that for certain gels, at high concentrations, the equation $\mathrm{E} = k_1\mathrm{C}^n$ holds over limited ranges, where E = Young's modulus, C = concentration, k_1 is a constant, and n is an index the value of which depends on the temperature of the system. See comments[3] and other developments.[4]

If the swelling agent penetrates into the micelles ' intramicellar ' swelling is said to take place ; if it merely penetrates between the different micelles 'intermicellar' swelling takes place. If the micelle is modified by virtue of a reaction between it and the swelling-agent, 'permutoid' swelling is said to occur.

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[1] *J. Chem. Soc.*, 1916, *109*, 307.

[2] *See* Loeb, *Proteins and the Theory of Colloidal Behaviour*, McGraw-Hill Book Co. (1922). Katz, *Trans. Farad. Soc.*, 1933, *29*, 279.

[3] *See*, for example, Donnan, *Chem. Rev.*, 1924, *1*, 87 ; Hill, *Proc. Roy. Soc. A.*, 1923, *102*, 705.

[4] *See*, for example, Northrop and Kunitz, *J. Gen. Physiol.*, 1927, *10*, 161, 893, 905 ; Kunitz, *ibid.*, 1930, *13*, 565.

It is found that thiocyanates and iodides, and a number of organic compounds such as resorcinol and thiourea, promote the swelling of proteins and polysaccharides.

Hysteresis. The term 'hysteresis', as used in colloid chemistry, sometimes refers to a gradual weakening of some specific property with repeated experimentation upon it (e.g. the progressive decrease of the rate of swelling of a gel with repeated drying and re-swelling, or the gradual lowering of the melting-point when a gel is repeatedly melted and re-solidified). The term is also used to indicate, for instance, that a difference exists between a setting-point and a melting-point (thus the melting-point (*q.v.*) of a 10 per cent 'hard gelatine' gel may sometimes be 5–10 degrees higher than its setting-point (*q.v.*), and in the case of agar-agar systems the 'hysteresis' may correspond to a range of 60 degrees between these two points).

Melting-points and Setting-points of Gels. The melting-point of a gel is the temperature at which the gel-sol transformation takes place, while the setting-point is the temperature at which the sol-gel transformation occurs. In practice these temperatures are not sharp (*see* method of measurement), nor can they be said to have equal values, as the setting-point is usually lower than the melting-point (*see* Hysteresis above).

Schröder Paradox.[1] The 'Schröder paradox' is an apparent contradiction of the Second Law of Thermodynamics due to the observation that a gelatine xerogel will swell more when in contact with liquid water than when in contact with water vapour at the same temperature. Von Schröder concluded that the vapour pressure of the water in the swollen gelatine must be greater than that of pure water, since on raising the swollen gel into the vapour phase water will distil to the plane surface of the water in the containing vessel. If the vapour-swollen gel can still exert some swelling-pressure in liquid water, the phenomenon might be used to convert heat-energy isothermally into work—hence the paradox. The facts are in dispute, and careful repetition of the work will be necessary before any definite decisions can be made.

Diffusion Constant (Diffusion Coefficient). *See under* Micellar Weight.

Sedimentation Velocity Constant. *See under* Micellar Weight.

Liesegang's Rings (Rhythmic Banding). Liesegang coated a glass plate with a layer of gelatine which contained a small proportion of potassium dichromate. When a drop of concentrated silver nitrate solution was placed on the gelatine surface, the silver nitrate diffused throughout the surface-layer and reacted with the potassium dichromate to form silver dichromate. This latter substance (or rather the silver chromate into which it readily changes), however, did not appear as a continuous precipitate, but settled out in the form of concentric rings (Liesegang's Rings or Rhythmic Banding—*see* Preparations later). It has been shown that the use of colloids is not essential to the occurrence of the phenomenon.

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[1] Von Schröder, *Z. physik. Chem.*, **1903**, *45*, 109.

Various explanations of the phenomenon, none entirely satisfactory, have been put forward. Ostwald suggested that as the silver nitrate diffuses through the film, silver chromate is formed, and this also moves forward in the form of a supersaturated solution which gradually increases in concentration as it moves until a position is reached where the solution-system breaks down and precipitation commences, the material in excess of that which would saturate migrating to the position in which the crystals have started to appear. The net result is the appearance of a ring or band. By repetition of this process alternate gaps and bands are produced.

Bechold held that the material to be precipitated is slightly soluble in the reaction-products, and that the bands will form only in those places where the concentrations of such products have become sufficiently reduced. Bradford held that the banding is due to gradual adsorption of the solute in the gel by the growing precipitate. Holmes attributed the phenomenon to conditions governing the rate of diffusion. In this explanation it is pointed out that according to Fick's Law of Diffusion the rate of diffusion is maximum where the difference in concentration in two contiguous layers of the ions concerned is greatest. Consequently, the region near the band decreases in concentration of negative-ion faster than does the region more remote. Finally the positive ions have to advance some distance beyond the band to meet a concentration of negative ions such that the product of the ionic concentrations would overreach the solubility-product of the substance to be precipitated, and when such a condition arises a new precipitation-band is formed. When band-formation is attempted in the presence of a gel, the nature of the gel sometimes exercises a marked influence on the result. For instance, lead chromate forms bands in an agar gel but not in a gelatine gel.

Double Refraction. If, for example, a suspensoid sol be placed in a suitable hollow triangular prism, and a beam of polarized light passed through the system (entering at one of the plane faces), ordinary refraction and consequent deviation will occur. If the sol is caused to *flow* through such a prism while the beam is still passing through the system, in some cases no change in optical phenomena is observable, but in other cases a secondary extraordinary refracted ray is obtained. The phenomenon is called 'stream double refraction' ('streaming birefringence'), and is caused by orientation of the particles in the direction of the flow. Occasionally, double refraction can be produced by subjecting the sol system to the influence of a magnetic field; such a phenomenon is termed 'magnetic double refraction'. When such a phenomenon occurs it may sometimes be possible to obtain, through its investigation, information on the shape of the individual particle (e.g. whether the particle is rod-shaped, &c.).[1]

Electrosmosis and Electrophoresis. The phenomena of Electrosmosis and Electrophoresis and the concept of ζ-potential are usually associated with Colloid Chemistry. These terms may be defined as follows:

Electrosmosis. When, through the agency of an applied E.M.F., a liquid moves in a stationary capillary, or in a capillary system, the phenomenon is termed 'electrosmosis'.

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[1] *See* Article by Edsall, 'Advances in Colloid Science' (Vol. I, p. 269). Interscience Publishers Inc. (New York), 1942.

Electrophoresis. When, on account of an applied E.M.F., particles dispersed in a liquid move, relatively to the 'continuous' liquid, towards one of the electrodes, the phenomenon is termed 'electrophoresis'. (*Note.*—'Cataphoresis' was the older term, but as migration towards the anode has been observed in the cases of certain particles, the newer term is now generally applied.)

ζ-potential (zeta-potential). 'The energy required to transfer an electron from the outer phase to the plane where a shift takes place in case of electrophoresis.'[1]

In studies on colloids two other phenomena are encountered, viz. 'streaming-' or 'flow-potential', and 'sedimentation-potential'. When an E.M.F. is set up due to the mechanical forcing of a liquid through a stationary tube, such an E.M.F. is termed a 'streaming-potential'. When an E.M.F. is set up between the upper and lower surfaces of a liquid due to the dropping of solid particles through the liquid (Dorn Effect), the E.M.F. thus developed is called a 'sedimentation-potential'.

Helmholtz and others attributed these electrokinetic phenomena to the existence of electrical 'double layers',[2] which somewhat resembled parallel-plate condensers. Later, the idea of 'diffuse double layers' was developed.[3]

For example, in the case of a solid surface in contact with a liquid, the charge on the solid surface was imagined to be embedded in the surface and to constitute the inner stratum of the double layer. The charges in the liquid were imagined to be distributed in such a way that the double layer extended to considerably more than molecular distances into the liquid. Similar observations are made, for instance, in the case of the oil globules in oil hydrosols. Fig. 14 (XV^3) is an illustration of the concept of a diffuse double layer in such a case. Freundlich (1926), discussing the nature of the interface between a solid and a liquid, assumed that in moving the two phases relatively to each other the surface of separation is not identical with the true interface. He assumed that a thin film of liquid adheres firmly to the wall of the solid phase. Whilst the Nernst (thermodynamical) potential is the true potential difference between the two phases, the ζ-potential (electrokinetic potential) is the potential difference between the internal portions of the movable part of the liquid and the surface of separation (i.e. that surface of the thin 'adhering' film which is nearer the movable part of the liquid). The values of the Nernst potential (ε) and the electrokinetic- or ζ-potential are thus identical.

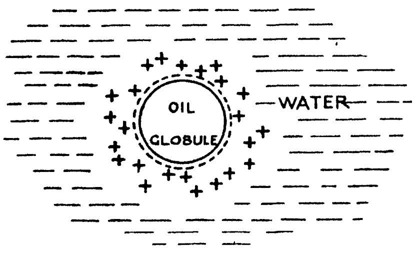

FIG. 14 (XV^3)
Diffuse double layer

To illustrate qualitatively the inter-independence of the values of the

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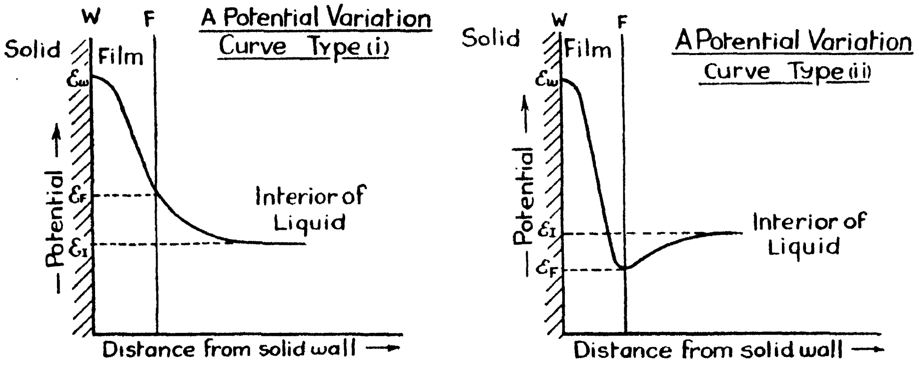
[1] Eilers and Korff, *Trans. Farad. Soc.*, 1940, *36*, 230.

[2] *See*, however, Laing, *J. Phys. Chem.*, 1924, *28*, 673, and McBain and Laing-McBain, *Z. physik. Chem. A.*, 1932, *161*, 279.

[3] Guoy, *J. Phys.*, 1910, *9*, 457. *See* also Debye and Hückel, *Physik. Z.*, 1923, *24*, 185; Stern, *Z. Electrochem.*, 1924, *30*, 508; Freundlich, *Kapillarchemie* (Leipzig, 1930).

Nernst potential (which is sometimes called the 'galvanic' potential) and the ζ-potential, the following diagrams (modifications of a diagram due to Smoluchowski), Figs. 15 (XV^3) and 16 (XV^3), are given, the film of liquid which adheres to the wall of the solid being represented by the distance WF.



FIGS. 15 (XV^3) and 16 (XV^3)
Diagrams showing relationship between values of the Nernst potential and the ζ-potential

ε_W = potential of the solid wall, W
ε_I = potential of the interior of the liquid
ε_F = potential at the surface, F, where a 'break' takes place in electrokinetic processes

In either case, the value of the Nernst galvanic potential (ε) would be given by $(\varepsilon_W - \varepsilon_I)$, and the value of the ζ-potential by $(\varepsilon_F - \varepsilon_I)$. It is clear that the value of the one could, in general, be different from the value of the other, and that they may differ even in algebraic sign. Stern [1] developed a theory of ζ-potential, and gave equations for the evaluation of the potential-gradient from the edge of the particle out into the liquid. Insufficient information, however, is forthcoming concerning several of Stern's factors to allow the equations in question to be applied with confidence. Stern's theory implied that the curves within the film-region, WF, would be straight lines. (*See* paper by Audubert (translated by Craxford), *Trans. Farad. Soc.*, 1940, *36*, 144.) For other views on the electrical double layer and on ζ-potential *see*, for example, the contributions of Müller [2] and von Buzagh.[3] For reviews of electrokinetic theory, *see* Horwitz,[4] and a collection of papers, *Trans. Farad. Soc.*, 1940, *36*, 1–322. Also *see* General Discussion on collected papers, *Trans. Farad. Soc.*, 1940, *36*, 711–32 (*see* p. 394).

Much discussion is still taking place as to the nature of ζ-potential. Its value is measured by the use of theoretical electrokinetic formulae. Formerly Perrin, and others, by simple treatment, found that for a bundle of capillaries:

$$V = \frac{IK\zeta}{4\pi\eta\kappa_l} \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

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[1] *Z. Elektrochem.*, 1924, *30*, 508.
[2] *Kolloidchem. Beihefte*, 1928, *26*, 257.
[3] *Kolloid-Z.*, 1930, *52*, 46.
[4] *J. Chem. Ed.*, 1939, *16*, 519.

where V $=$ volume of liquid transferred by electrosmosis, the temperature being constant
η $=$ coefficient of viscosity of the liquid
I $=$ current strength
K $=$ dielectric constant of the medium between the 'plates', if the double layer were simply regarded as being of the condenser type
κ_l $=$ specific conductivity of the liquid system in the capillaries

For the streaming potential, E, when a liquid is mechanically forced through a capillary, it was deduced that

$$E = \frac{PK\zeta}{4\pi\eta\kappa_l} \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where P $=$ applied pressure, the other symbols having the same meaning as in Equation (30). These formulae were based on the assumption of the existence of the simple double layer. The velocity, v, of a suspended particle, due to electrophoresis, was held by Smoluchowski to be independent of particle-shape. According to Debye and Hückel,[1] however, it is given by:

$$v = k\frac{XK\zeta}{\eta}$$

or, if X and ζ be expressed in volts,

$$v = k\frac{XK\zeta}{300 \times 300 \times \eta} \quad . \quad . \quad . \quad . \quad . \quad (32)$$

where X $=$ potential gradient of applied E.M.F., and k $=$ a constant for particles of a given shape.

In the case of particles of cylindrical shape the value of k would be $\frac{1}{4\pi}$. For particles of spherical shape the value of k, according to Hückel, would be $\frac{1}{6\pi}$. Henry [2] showed that the latter conclusions would be valid if the particle had the same conductivity as the medium, while for insulating particles the value of k is independent of particle-shape.

Henry (*loc. cit.*) introduced an important modification in electrophoretic mobility formulae. His modified version has since been extensively applied. The modification consisted essentially of the introduction of a rather complex correction-factor $f(\kappa r)$, where r is the radius of the charged particle (if a droplet) and κ is the reciprocal of the effective thickness of the double layer. Curves are given which enable $f(\kappa r)$ to be calculated. According to the new equations, the electrophoretic mobility, u (*see* meaning, p. 442), is given by the equation:

$$u = \frac{K\zeta}{4\pi\eta}.f(\kappa r),$$

and the charge density, in e.s.u. per sq. cm., is given by the expression:

$$\frac{u\eta(1 + \kappa r)}{r}.\frac{1}{f(\kappa r)}.$$

Kemp [3] has given a review of mathematical treatment of electrokinetic phenomena.

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[1] *Physik. Z.*, 1924, *25*, 49.

[2] *Proc. Roy. Soc. A.*, 1931, *133*, 106.

[3] *Trans. Farad. Soc.*, 1935, *31*, 1347.

SECTION 2: METHODS OF PREPARATION

The preparation of inorganic colloidal solutions can be divided into two main groups:

(1) Condensation methods
(2) Dispersion methods

Each of these main methods may be subdivided into various categories. These will be reviewed in some detail.

(1) **Condensation Methods.** In the methods under this heading the colloid is produced by the aggregation of molecules originally in true solution; this is accomplished by chemical methods. Chemical condensation methods include:

(*a*) **Reduction.** A number of typical preparations under this heading are recorded:

I. Preparation of Colloidal Silver by the Method of Carey Lea. (*See* Vol. II, Chap. V.)

II. Zsigmondy's Preparation of Standard Gold Hydrosol.[1] The following material is required: (A) water distilled twice over potassium permanganate, condensed in a condenser consisting of a block tin coil, and collected in thoroughly cleansed (but not wiped) vessels of resistance glass (*N.B.*—All glassware used in this connexion should be of the best 'resistance' type), (B) a solution containing 6 grams of hydrochloroauric acid ($HAuCl_4$, $3H_2O$) in conductivity water made up to 1 litre, (C) 1 litre of 0·18N potassium carbonate (purest) solution, (D) a 0·3 per cent solution of freshly distilled formaldehyde.

120 ml. of the water indicated in (A) above is heated in a 500-ml. beaker over a plain gauze, and 2·5 ml. of the solution of hydrochloroauric acid is added, followed by 3·5 ml. of the potassium carbonate solution. The mixture is then well stirred (a soft-glass rod should *not* be used) and heated to boiling. It is then removed from the heater, and 1·0 to 3·0 ml. of the formaldehyde solution quickly added with vigorous stirring. In much less than 1 minute the hydrosol develops an intense red colour. The sol should show a weak brownish opalescence to reflected light, and a clear bright-red colour to pure transmitted light; no trace of a blue or a violet shade should appear. Such suitable gold sols contain particles of 'diameters' from 20 mμ to 30 mμ. The sol may be dialysed against redistilled water, but will keep without this treatment in vessels of resistance glass.

Tannin solution freshly prepared (1 per cent in water) may also be used to prepare a gold sol. 100 ml. water is brought to the boil and 10 ml. of a 0·01 per cent gold chloride solution added in an Erlenmeyer flask. Small amounts of the tannin solution are added very slowly with intermittent stirring—an intense red colour is formed. Hydrazine hydrate, phenyl-hydrazine or hydroxylamine (in 0·5 per cent concentration) may also be used for the reduction).

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[1] Zsigmondy, *The Chemistry of Colloids*, 1917.

III. Kohlschütter Silver (*see* Vol. II, Chap. V). The walls of the vessel in which this sol is prepared exercise an interesting influence on the characteristics of the sol. If the vessel is of Jena glass, the sol appears brownish-red by transmitted light and greyish-green by reflected light. If a vessel of soft-glass or of quartz be used, the sol is brownish-yellow by transmitted light and greyish-black by reflected light. The sol cannot be formed in a platinum vessel which has been coated internally with platinum black.

IV. Metallic Sulphide Sols (*see* Vol. II, Chap. V). Examples:

Arsenious Sulphide Sol. A convenient method for the preparation of a sol of arsenious sulphide is to pass purified sulphuretted hydrogen to saturation through a solution of arsenious acid. A bright-yellow sol results. The excess sulphuretted hydrogen may be removed (*a*) by a stream of hydrogen, or (*b*) by boiling it off. The size of the micelles increases with increasing concentration of the arsenious acid, and decreases with increased speed of the sulphuretted hydrogen treatment, the temperature of the system being of minor significance. Freundlich and Nathansohn gave the following procedure for the preparation of an arsenious sulphide sol of high degree of dispersion: 40 to 100 ml. of a cold saturated solution of arsenious oxide is diluted to 200 ml., and then treated with a solution consisting of 1 ml. of water saturated with hydrogen sulphide which has been diluted with 100 ml. of water. A faint yellow colour develops. The system is then diluted to 1 litre with a solution of sulphuretted hydrogen ten times as concentrated as the one previously mentioned. Sulphuretted hydrogen is then led through the system to saturation. The excess of sulphuretted hydrogen is then removed by means of a current of hydrogen. The sol which results shows a very faint Tyndall cone.

Antimony Sulphide Sol. An orange-red sol of antimony sulphide may be obtained by passing sulphuretted hydrogen through a 0·5 per cent aqueous solution of tartar emetic (potassium antimonyl tartrate), followed by dialysis.

Mercuric Sulphide Sol (*Linder and Picton*). Hydrogen sulphide is led through 50 ml. of a 2 per cent solution of mercuric chloride (made by dissolving the mercuric chloride in water slightly acidulated with hydrochloric acid). The precipitated sulphide is filtered off, and washed free of chloride-ion. The precipitate is then suspended in 250 ml. of water and is peptized by leading hydrogen sulphide through the system for a period of about 2 hours. The resultant sol is black and opaque. Removal of the hydrogen sulphide by means of a current of hydrogen leads to a decrease in stability.

V. A Platinum Sol. Make 500 ml. of a 0·1 per cent solution of hydrochloroplatinic acid (H_2PtCl_6) slightly alkaline by the addition of a little potassium carbonate. Bring the resulting solution to the boiling-point. Remove the flame, and add about 3 ml. of a 33 per cent solution of acrylic aldehyde. When the colour of the system changes to black, filter, dilute the filtrate with an equal volume of water, and then dialyse.

VI. Von Weimarn's Gold Sol. To 400 ml. of water at the boil add 30 ml. of a 0·1 per cent solution of hydrochloroauric acid ($HAuCl_4$, $3H_2O$). To the resulting solution add, drop by drop, 2 ml. of 0·05 M Rochelle salt, continuing the boiling. A blue gold-system will develop after a short interval and, after another short interval, the system will change to the more highly dispersed red gold condition.

(*b*) **Methods of Oxidation** (*see* Vol. II, Chap. V).

(*c*) **Methods of Hydrolysis.** *Ferric Oxide Sol.* It contains positively charged micelle. The hydrochloric acid resulting from the hydrolysis can be removed by dialysis. A negatively charged ferric hydroxide sol can be prepared as follows: A saturated solution of ferric chloride is added from a burette very slowly to 100 to 200 ml. of ammonium carbonate solution (2 N) with continuous shaking. The precipitate first formed dissolves and gives a deep red-brown clear liquid. This sol loses its negative charge on dialysis.

(*d*) **Decomposition of Unstable Compounds.** When sodium thiosulphate is decomposed by sulphuric acid a very unstable acid $H_2S_2O_3$ is probably formed and this immediately decomposes into sulphurous acid and sulphur. The sulphur separates in a colloidal form. The following preparations are illustrative:

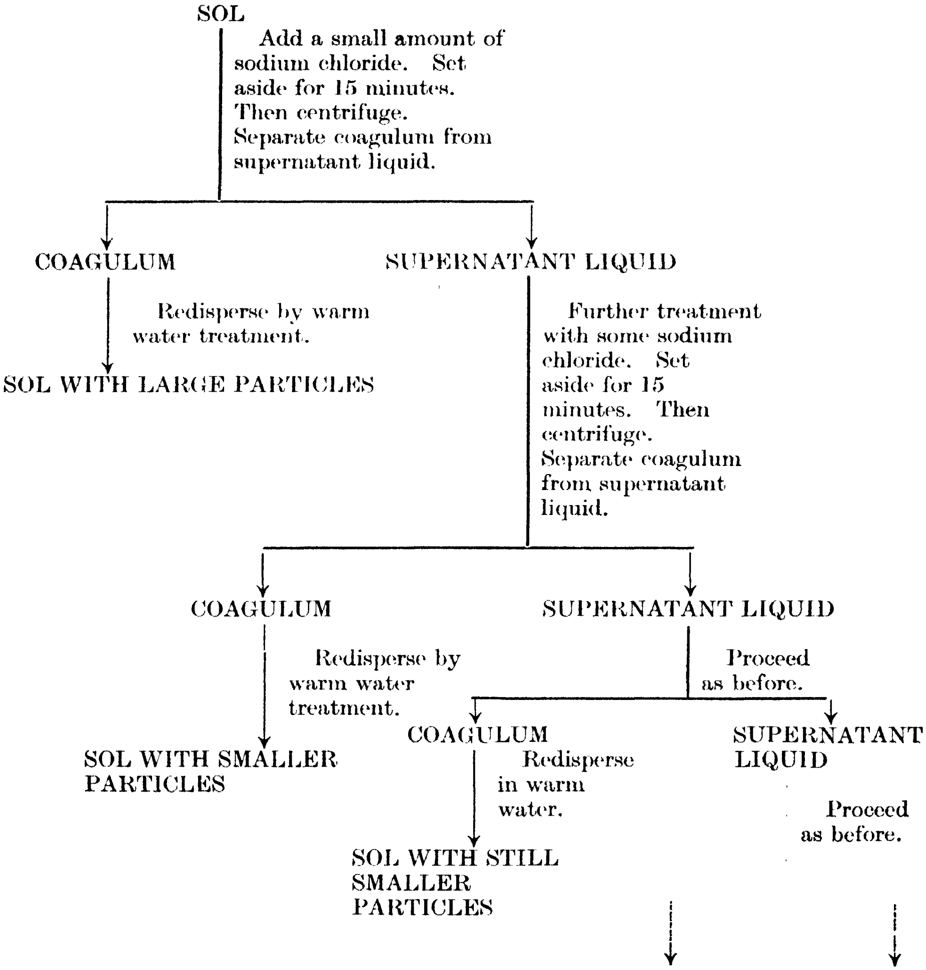
Sulphur Sol (*Oden*). To 10 ml. of 18 M sulphuric acid, constantly stirred and orginally at 25°, 30 ml. of a 3 M solution of sodium thiosulphate is added, drop by drop, the rate of addition being 2 ml. per minute. The temperature during the addition should not be allowed to exceed 50°, lest the reaction should become uncontrollable. A centrifuge-tube is recommended as the reaction-vessel, and a quantity larger than 100 ml. should not be prepared in one batch. After the addition of the thiosulphate solution, the mixture is cooled without delay and sufficient powdered sodium chloride is added to precipitate the sulphur. The mixture is then centrifuged, and the 'supernatant' liquid removed. The sulphur residue is then treated with water at about 80°, and part of the sulphur becomes repeptized. The mixture is again centrifuged to separate any sulphur which has coagulated irreversibly. The supernatant liquid, which should then be taken off, consists of a sulphur hydrosol.

The hydrosol prepared in the above manner is very polydisperse. It may be fractionated as indicated in the scheme shown on the next page. At lower temperatures less sodium chloride is needed to precipitate the sulphur. Purification of the sulphur may therefore be effected by using as little warm water as possible for the redispersion of the salted-out coagulum and cooling the resultant system to room temperature (or lower). A new coagulum is formed which, after centrifuging, &c., may be redispersed in warm water. Decrease in the salt-content of the sulphur hydrosols may be effected by electrodialysis. Such sols are hydrated and belong to the emulsoid category.

Alternative procedures for the preparation of a sulphur sol are as follows:

25 grams of crystalline sodium thiosulphate is dissolved in 15 ml. of water. 35 grams of concentrated sulphuric acid is placed in a 200 ml. beaker and the acid cooled to 0°. The sodium thiosulphate is added, very slowly, from a dropping-funnel to the acid. A very thick viscous yellow mass results. About 20 ml. of water is then added and the mixture heated on the water-bath for about 15 minutes to allow sulphur dioxide to escape. The clear yellow liquid that results is cooled and filtered through glass wool.

This colloidal solution still contains some thiosulphate, which can be partly removed by dialysis. A small amount, however, must be left or the colloid solution breaks down.


SOL
Add a small amount of sodium chloride. Set aside for 15 minutes. Then centrifuge. Separate coagulum from supernatant liquid.
COAGULUM
SUPERNATANT LIQUID
Redisperse by warm water treatment.
SOL WITH LARGE PARTICLES
Further treatment with some sodium chloride. Set aside for 15 minutes. Then centrifuge. Separate coagulum from supernatant liquid.
COAGULUM
SUPERNATANT LIQUID
Redisperse by warm water treatment.
SOL WITH SMALLER PARTICLES
Proceed as before.
COAGULUM
SUPERNATANT LIQUID
Redisperse in warm water.
SOL WITH STILL SMALLER PARTICLES
Proceed as before.

A sulphur sol may also be prepared by taking a very dilute solution of ammonium sulphide and neutralizing with dilute hydrochloric acid solution. Depending on the conditions, sols of different degrees of dispersion can be obtained.

Physical Condensation Methods include :

Freezing. By the rapid cooling of certain organic liquids containing water in solution, ice may separate as colloid particles. For example, if a saturated solution of chloroform and water is rapidly cooled to — 30° the ice separates in particles sufficiently small to pass readily through filter paper.

By change of Solvent. Selenium is soluble in carbon disulphide. If such a solution is poured into ether a bright red colour is produced—due to the formation of a colloidal solution of the selenium in ether.

A stable sol of sulphur with a bluish-white appearance is obtained by adding with vigorous stirring a solution of sulphur in alcohol (solubility 0·05 per cent) into a large volume of water. Similar types of sols can be prepared with phosphorus and gamboge using various solvents.

(2) **Dispersion Methods**

The dispersion of aggregates can be accomplished in various ways, e.g. by: (*a*) mechanical, (*b*) chemical or (*c*) electrical methods.

In some instances more than one of these actions may operate at the same time. This especially applies to the combination of mechanical and chemical forces. This action is known as dispersion or peptization. The latter term was originally introduced by Graham, since the process was somewhat similar to that observed when proteins are peptized by means of organic ferments. These three methods will be studied separately.

(*a*) **Mechanical Dispersion.** At one time most methods of bringing about dispersion depended on electrical or chemical treatment and very few processes utilized mechanical treatment alone. In recent years, however, this method has developed and many disperse systems now depend on such technique. Solid material may in some cases be reduced to a very fine state of division by prolonged grinding alone. The extreme degree of fineness is best secured by 'diluting' the material with some other solid which can finally be removed by an indifferent solvent. The remaining material when shaken up with the dispersion medium disperses spontaneously if the grinding has been fine enough. Wegelin has produced sols of silicon, vanadic acid, molybdic acid, and a few other compounds by grinding in an agate mortar, sometimes with the addition of a little water. With substances such as copper, copper oxide, sulphur, graphite he was unsuccessful. Kuzel by intense grinding of tungsten, silicon, zirconium, &c., followed by an acid and alkali treatment also obtained dispersions. As early as 1906 von Weimarn obtained dispersions by mechanical grinding or shearing action. He introduced a stabiliser to exert a protective action on the particles produced. His method, however, appears to have met with little success and mechanical grinding and shearing methods were little used until Plauson introduced the so-called Colloid Mill.[1] In the original type of apparatus, lugs on a beater drum revolving at 3,000 or more revolutions per minute passed grooves notched in stationary baffles and the coarse particles present in the aggregate were separated into smaller particles. The mill is described in Vol. II, Chap. V.

By very rapid mechanical movement and with only slight clearance between the surfaces it is possible to bring about the mechanical dispersion of material. The dispersed substance under good conditions gives particles of an average size of 1 μ. This is many times the diameter of true colloidal particles so that such mills should more appropriately be called dispersion mills rather than colloid mills. A beater mill has the objection that, with increased speeds, the resistance of the air increases and a considerable amount of heat is evolved. It is also difficult to make certain that some relatively coarse material (not properly dispersed) does not pass the beaters.

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[1] *Chem. Ztg.*, 1920, *44*, 553, 565.

According to Travis [1] a so-called Colloid Mill does not actually grind or break down solid particles to any extent. What it does accomplish is the deflocculation of particles, originally discrete, which have formed loose aggregates on packing. The mill disperses these aggregates in the presence of a liquid but it does not disintegrate the material. The mill is also of importance in the formation of emulsions.

At the present time there are many types of dispersion mills and these can be classified as follows:

The Beater type. In this type the solid and liquid are lead through a vertical hollow shaft between rapidly rotating hard discs. Under the action of friction the solid material is dispersed. The original Plauson Mill and the Oberberg are of this type.

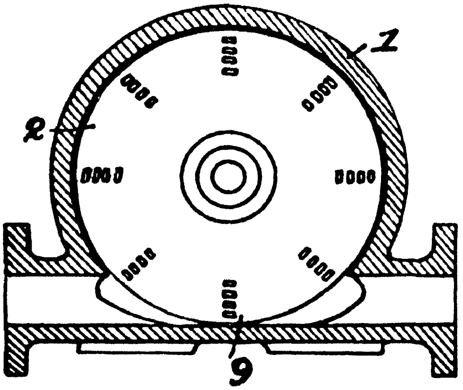

FIG 17 (XV[3])

Front view

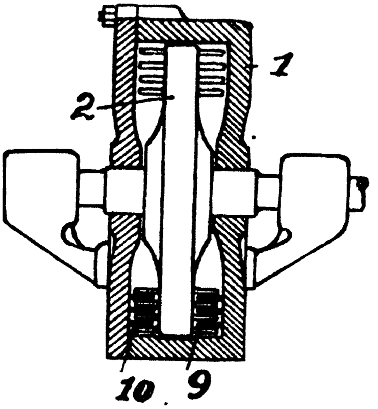

FIG. 18 (XV[3])

Side view

Oberberg Mill (schematic)

Smooth Surface Type. In this the dispersion is brought about by a hydraulic shearing effect set up by the action of a surface carrying a liquid film moving at a very high speed over a stationary surface. The adsorption of films of liquid upon the surfaces cause a great shearing stress in the rest of the thin layer of liquid between them. Representatives of this type are the Premier and Hurrell Mills as well as a mill known as the English Plauson.

Rough Surface Type. The grinding-surfaces here are rough or grooved and so a rapid turbulence is set up which intensifies the shearing action. The Charlotte Mill is in this class.

Combined Smooth and Rough Surface Type. This type gives very good dispersion but the clearance cannot be adjusted as readily for wear as in other models.

Other Types. While the Plauson Mill may still be used on the Continent especially for emulsion formation and for the dispersion of comparatively soft materials, other types are extensively used in England and America. The power requirements of the original apparatus were comparatively high and the fact that it mainly operated as a ‘ batch ’ machine was not in its favour. While the results as regards disintegrated products were very good, attempts were made to obtain other mills using less power. The Oberberg machine, for example, claimed to require only one-seventh of the original Plauson Mill for equal capacity. The Oberberg design[1] is schematically represented in Figs. 17 (XV^3) and 18 (XV^3). The mill chamber with the exception of the beating-point is empty so that in contra-distinction to other types of mill there is no rotation of the material within the housing (notation 1 in diagram). Notation 2 shows the rotor, 9 the beater, and 10 the baffle or anvils.

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[1] *Ind. and Eng. Chem.*, 1929, *21*, 423.

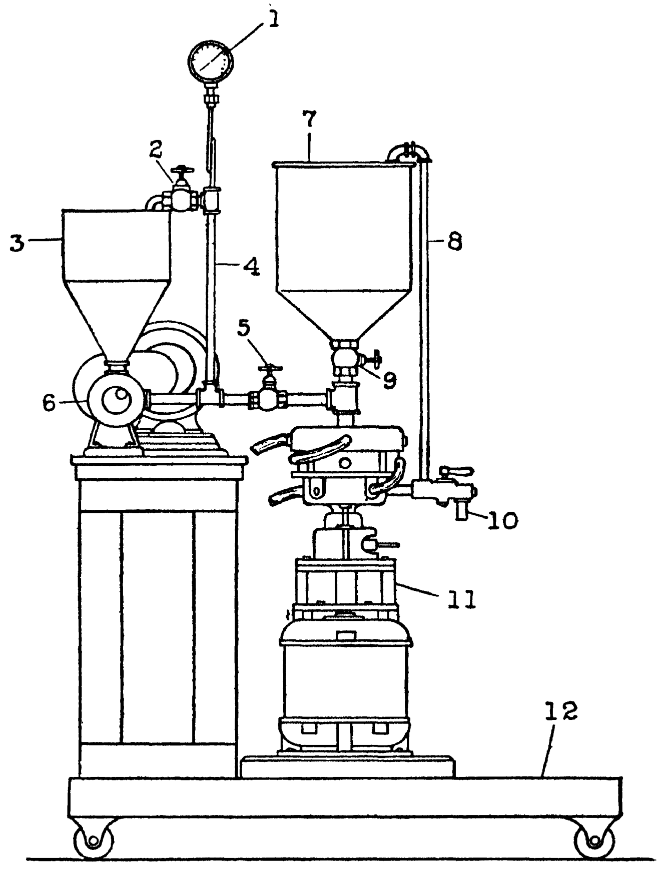

FIG. 19 (XV^3)
The Eppenbach mill

In the U.S. Colloid Mill[2] two flat grinding-disks are employed revolving in opposite directions. The rotors are 0·001 to 0·005 inches apart and intensive shearing action can be secured.

The Eppenbach Mill (heavy-duty portable model) works at very low clearance (0·5 μ) and at low peripheral speeds. The arrangement of the plant can be seen from the outline diagram (Fig. 19 (XV³)). The notation is as follows : 1, pressure gauge ; 2, pressure by-pass valve ; 3, pressure-feed hopper ; 4, pressure by-pass ; 5, pressure-feed valve ; 6, pressure pump ; 7, direct feed hopper ; 8, direct feed by-pass ; 9, direct feed valve ; 10, discharge faucet ; 11, water-cooled mill ; 12, portable base. The apparatus is water cooled. The arrangement of the turbines which cause great turbulence under pressure acts as a highly efficient pre-mixing element. The pressure is utilized for thrust, which eliminates ball-bearing thrusts and makes it possible to use relatively low horse-power.

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[1] *Ibid.*, 1928, *20*, 413.

[2] U.S. Colloid Mill Corporation, N.Y.

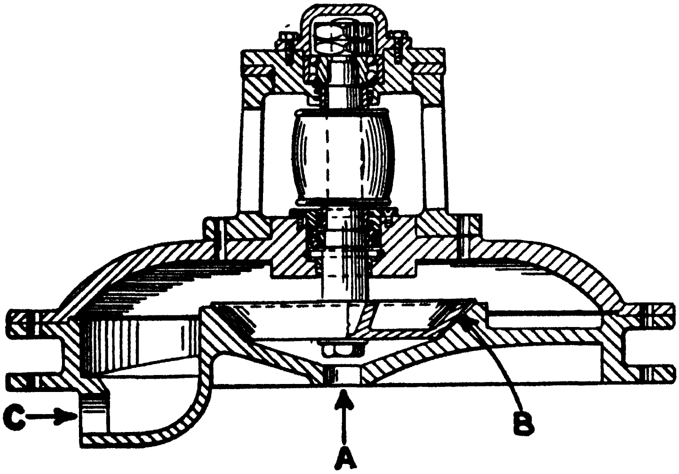

FIG. 20 (XV³)
Centrifugal smooth-surface type of mill

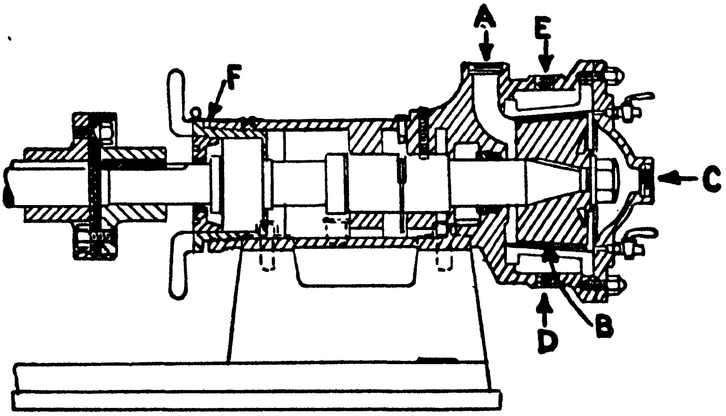

FIG. 21 (XV³)
A rough-surface type of mill

A centrifugal smooth-surface type of dispersion mill is shown in Fig. 20 (XV³). It has been described by Travis.[1] It has a truncated cone within a fixed cone rotating in opposite direction. The material is fed in from the bottom at A, passes between the working surfaces (B) and is thrown off at the top owing to the increase in centrifugal force as the diameter of the rotating surface increases. The outlet is at C.

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[1] *Ind. and Eng. Chem.*, 1929, *21*, 42.

Rough Surface Type. The working surfaces in this type are very similar to that of the centrifugal smooth surface type. The only difference is in the roughened surface. Fig. 21 (XV^3) shows in cross-section a mill in which the conical working surfaces covered with grooves are used.[1] Travis also has described a mill that embodies features of both the smooth-surface and rough-surface type the so-called turbine-type machine. It is shown in Fig. 22 (XV^3). A shows the material inlet, B the working surface and C the material outlet.

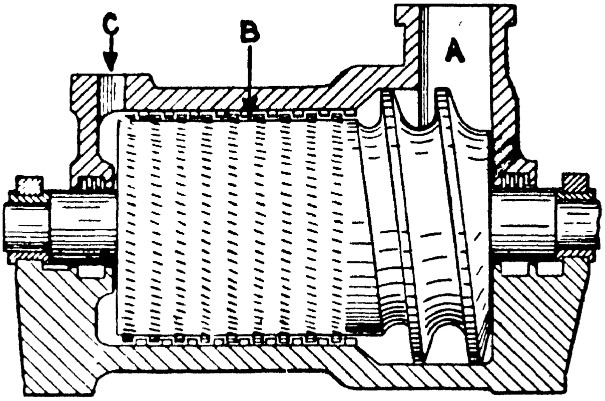

FIG. 22 (XV^3)
Turbine-type machine

The Premier Colloid Mill is extensively used and several types are available. The 5-in. horizontal type [2] has a rotor consisting of a smooth surface upon the frustrum of a cone. The surface of the stator is an integral part of the removable casing. The clearance is small and grinding to a very fine limit can be secured. The normal speed is about 9,000 revolutions per minute. In another Premier Mill of the vertical type the drive is direct from a vertical motor through a coupling. The apparatus is jacketed for thermal control. The normal speed is 3,000 revolutions per minute and with a ½ h.p. the output is approximately 50 lb. per hour. In the Premier Corrugated Mill [3] the faces of the stator and rotor have **V**-shaped corrugations so adjusted that the space between the grinding surfaces is less than the cross-sectional area of the space at the centre.

In the Charlotte Mill a grooved conical rotor is employed. It rotates within a correspondingly grooved conical stator with an adjustable clearance. Speed 3,000 revolutions per minute. This mill uses both hydraulic shear and impact action.

(*b*) **Chemical Methods.** *Ferric Hydroxide Sol.* To 100 ml. of a 5 per cent solution of ferric chloride in water add slowly a dilute solution of ammonia in water until the supernatant liquid is slightly red. Wash the ferric hydroxide precipitate several times by decantation. Drain the precipitate on a filter. Add the precipitate to 40–50 ml. of distilled water and shake vigorously. Pour about 5 ml. of this viscous liquid into 100 ml. of distilled water. Add a few drops of dilute hydrochloric acid solution (approximately 0·1 N) and shake. The colourless liquid gradually becomes brownish red with hydrosol formation. The addition of the calculated amount of hydrochloric acid will cause complete dissolution of the precipitate and the hydrosol becomes intense red on standing.

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[1] Travis, *loc. cit.*

[2] B.P., 221, 422, 221, 548/1923.

[3] B.P., 432, 570/1934.

Cadmium Sulphide Sol. From a soluble cadmium salt the sulphide is precipitated by hydrogen sulphide from an ammoniacal solution. The precipitate is filtered off, washed, and then suspended in a large volume of water and hydrogen sulphide passed through the mixture. The suspension first becomes milky and finally gives a golden yellow sol with a slight red shade on the surface. If the dissolved hydrogen sulphide gas is replaced by an inert gas, e.g. nitrogen, a stable sol results.

Vanadium Pentoxide Sol. 3 grams of ammonium vanadate is triturated in a mortar with 2 or 3 drops of dilute hydrochloric acid solution. The precipitate formed is washed repeatedly with distilled water and then placed in a flask with 150 ml. water and the mixture stirred. The solution darkens and after 2 hours is a dark red colour which shows clear to transmitted light.

(*c*) **Electrical Methods.** Of electrical methods of preparation that of Bredig is best known. This consists in the formation of a direct-current arc under water, using the metal as electrodes. The latter are disintegrated and colloidal solutions result. From 30 to 40 volts and 5 to 10 amperes may be used, e.g. in the preparation of colloidal lead, a lead plate with a binding post may be the anode, and a lead wire 1–2 mm. diameter, the cathode. Both electrodes are immersed in a dilute solution of sodium hydroxide solution (1 per cent) using D.C. 220 volts. The lead wire disintegrates to form black particles of colloidal lead.

For working conditions *see* Vol. II, Chap. V.

Bredig platinum sols have been prepared by Mindel and King [1] by arcing in air, oxygen, and nitrogen. The composition and stability are only affected to a very small degree by alterations in the dispersion medium or in the nature of the gases. Coagulation with acids does not alter the platinum content of the micelle. These sols are similar to normal Bredig sols in colour, electric charge, permanency and catalytic effect.

Some further preparations connected with Colloid Chemistry are now given :

Approximately Isoelectric Gelatine (*Loeb's Method of Preparation*). 50 grams of powdered commercial gelatine (which had a *p*H-value of 6·0 to 7·0) was placed in 3,000 ml. of N/128 acetic acid solution contained in a jar and maintained at 10°, being frequently stirred. After 30 minutes the supernatant liquid was discarded and fresh N/128 acetic acid at 10° added to make up the original volume. The mass was again frequently stirred and, after a further 30 minutes, the acetic acid solution was again decanted and replaced by an equal volume of distilled water at 5°. The gelatine was stirred and filtered through towel-cloth in a Buchner funnel using suction. It was washed in the funnel with five separate quantities each of 1,000 ml. of water at 5°, and drained. The gelatine was transferred to a large beaker which was heated in a water-bath to approximately 50° until the gelatine melted. The concentration of the gelatine was determined by evaporating 10 ml. of the molten substance in an electric oven for 24 hours at from 90° to 100°. 100 ml. of a 1 per cent gelatine solution prepared in this way contained no more than 0·001 gram of ash.

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[1] *J. Amer. Chem. Soc.*, **1943**, *65*, **2112**.

Conversion of Gelatine into 'Gelatose'. Subject a 10 per cent sol of gelatine to prolonged boiling, replacing any water that may be evaporated. Test the condition of the system occasionally by removing small samples and placing them on a clean, cold, glass surface. When eventually a sample will not gel on cooling, the gelatine has been hydrolysed to 'gelatose'. This characteristic of gelatose (inability to gel) is noteworthy.

Preparation of a Thixotropic Gel: To 30 ml. of a 5 per cent dialysed iron, in an 8-inch Pyrex test-tube, add 3 ml. of a 2 per cent solution of sodium hydroxide (A.R.), and shake thoroughly. The setting-time of the gel which results is about 1 minute. The setting-time may be varied by changing the relative volumes of the sodium hydroxide and the dialysed iron, or by replacing the sodium hydroxide by another electrolyte, e.g. potassium chloride.

Preparation of Gelatine Sol. Gelatine is sold in leaf, foil, and powdered form. A high-grade product (e.g. Nelson's 'Crystal Leaf', or Coignet's 'First Quality' and 'Photographic') is desirable for most work. A quantity of the chosen brand, sufficient for all investigations on hand, should be purchased at the commencement of the series of experiments, and for any one experiment the sample chosen should be representative of the stock as a whole (i.e. sampling should be random). When merely *reproducible* (as distinct from *quantitative*) results are desired it is convenient to prepare the sols on the basis of weight gelatine/volume water. If the leaf form be used it should be broken into pieces each of area about ½ sq. in. The pieces are then placed in a beaker, and *covered* with cold water at any fixed arbitrary temperature, any air bubbles which appear being removed by stirring or by shaking. Gelatine imbibes about 10 times its own weight of water, so that, for example, if the amount of water used does not exceed this quantity there should be no unimbibed water when swelling is complete (after about 30 hours). The gelatine is allowed to swell to completion, changing the water occasionally (*N.B.* the edges of the leaf swell more slowly than the central portion ; care should therefore by taken to allow them to soften adequately), or alternatively the gelatine may be allowed to swell under the given conditions for a fixed arbitrary time (not less than 3 hours). It should be remembered that gelatine sols and gels (in common with sols and gels of some other substances) possess a considerable degree of '*memory*', i.e. the properties of the system will depend not only on the temperature and concentration of the system, but also on the previous history, e.g. time and temperature of swelling, temperature of sol-formation, duration of sol-formation. The next process is the dispersion of the gelatine from the gel to the sol system. The beaker and contents may be heated over the water-bath to a temperature of about 40°, but it is usually desirable to heat to a higher temperature (e.g. for filtration purposes—if filtration be deemed necessary—a temperature of 90° may be needed to reduce viscosity adequately). The practice is often followed of heating the sols at 100° for an arbitrary period (e.g. 5 minutes) for the purpose of eliminating, as far as possible, differences in previous history of samples, then cooling at a definite arbitrary rate to the temperature at which it is desired to use the sol, and maintaining the system at this lower temperature for a fixed arbitrary time before experimentation upon the sample is commenced. It is, however, recommended to follow rigidly and in detail any particular conditions of procedure which may be decided upon in advance, if the results of a series of investigations are to be used for comparative purposes. In some cases a sol prepared as above indicated will not require filtration since the gelatine may be regarded as completely dispersed, but in other cases (e.g. when a salt which is capable of forming a precipitate with calcium salts, chlorides, sulphates, or sulphites has to be added) filtration will be necessary. The original Chardin paper (or any good imitation of it) may be used. The paper should be cut and made into a fluted filter, particular attention being paid to the 'apex' (point) of the filter (twelve folds are sufficient). A hot-water funnel with a short stem (just projecting below the stopper) passing through a thin stopper ($\frac{3}{4}$ in. or less in length) at the base of the water-bath should be used, and the temperature of the bath should be regulated so that the rate of filtration is reasonable. Too high a temperature is to be avoided, however.

If the gelatine gel (which forms on the cooling of suitable sols) is needed for examination of its optical or elastic properties, the gel should be allowed to stand for about 5 hours after the setting is apparently complete, since accidental birefringence and its modulus of elasticity do not reach steady values unless time of standing is allowed. If it is required to make gels of a particular shape (e.g. cylindrical, conical, &c.), moulds of Pyrex glass tubing, tin-foil, or of wood lined on the inside with tin-foil, the tin-foil being lightly smeared with vaseline (excess of the vaseline being removed by cotton-wool), may be used. The gel may be removed from a cylindrical glass tube (which has been stoppered at one end during the filling) by dipping the tube for a brief period into hot water and then allowing the gel to fall from the tube into an adequate depth of cold water.

Preparation of Silicic Acid Gel. Dilute some water-glass until its specific gravity is about 1·15. Prepare an equal volume of 6 N hydrochloric acid. Pour the water-glass solution into the acid solution. Mix the liquids rapidly, and then allow the mixture to stand at room temperature. The reaction may be written :

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$$

A bluish opalescence develops, and the sol sets to a hydrogel after about 1 hour. If the original silicate-solution were very dilute, difficulty would be experienced in making the gel set. The difficulty could then be overcome by evaporation until the resultant liquid contained about 15 per cent of silicic acid—the gel would then set on standing at ordinary temperature. The salt may, if so desired, be mainly removed by breaking the gel into small pieces and washing with water.

For the preparation of larger quantities of silicic acid sol, the water-glass and hydrochloric acid solutions may be run simultaneously at equal slow rates into a vessel equipped with a good mechanical stirrer, allowing the contents to overflow continuously into a suitable receiver. The product is then set aside for gel-formation. The salt may then be washed out.

Silicic acid gels may, in general, be represented by the general ‘ formula ’ SiO_2, nH_2O, where n may have values from 300 down to 0·5 (approximately). Reduction in the value of n may be accomplished by various methods of drying, e.g. (*a*) by washing with 90 per cent alcohol, (*b*) by washing with absolute ether, (*c*) by evaporation, *in vacuo*, at room temperature, or over sulphuric acid. When $n \fallingdotseq 300$, the gel flows together again after being broken into pieces. When $n \fallingdotseq 40$ to 30, the gel is sufficiently rigid to stand alone, and it may be cut. When $n = 6$, the gel gives an apparently dry powder on being pulverized. When $n =$ from 3 to 1·5, the gel becomes opaque and chalky, but when $n < 1$ the gel clears again. The ‘ silica gel ’ of commerce[1] is a dried material sold in small lumps, containing sorbed water to the extent of about 16 per cent. Before use as a sorbing agent, this material should be activated by being heated in a stream of dry air at from 150° C. to 300° C., care being taken not to reduce the water-content below 5 per cent (lest the porous structure be affected). It should then be put in suitable containers for immediate use, or else properly stored so as to protect it from gases, moisture, &c., until it is required. Silica gel, in aluminium perforated containers is, for instance, often placed as a drying agent in cases containing Analytical Balances. Commercially it has a variety of uses, e.g. in the drying of air for blast-furnace work, as a support for the finely divided platinum in the Contact Process for the manufacture of sulphuric acid, and in the removal of valuable hydrocarbon petrol-vapours from natural gas.

Gels of silicic acid, when of suitable concentration, vibrate when the glass tube containing them is tapped. The frequency of the vibration is substantially proportional to the inverse of the internal diameter of the vessel and is independent of its length.[2]

Liesegang's Rings—*Silver (Di)chromate Rings.* Disperse 4 grams of commercial gelatine in 100 ml. of distilled water (an ordinary commercial gelatine is best ; for good results in ring-formation the gelatine should contain a trace of gelatose (see Preparation) and a trace of acid. Commercial gelatine usually contains these constituents in adequate proportions. If a high-grade gelatine be used, it may be necessary to add about 8 drops of a 5 per cent solution of citric acid and/or of gelatose to the 100 ml. of the sol. If too great an excess of the ‘ impurities ’ be added, however, a continuous precipitate, not banded, may be produced). To the 4 per cent gelatine sol add 2 ml. of a concentrated solution of potassium dichromate and mix well. Pour the mixture on the centre of a de-greased, well-cleaned, slightly warmed glass plate held in one hand about 2 inches above the horizontal surface upon which the plate will eventually rest. The glass plate may be slightly tilted, according to circumstances, so that a thin layer of the mixture (about

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[1] For a method of preparing porous silica gels *see* Holmes, *Ind. and Eng. Chem.*, 1925, *17*, 280. *See also* W. Partick, U.S. Patent 1,297, 724 (1919).

[2] *See* Holmes, Kaufmann, and Nicholas, *J. Amer. Chem. Soc.*, 1919, *41*, 1329.

0·5 ml. per sq. inch of glass surface) is formed on the plate. Some practice is necessary for success in the coating of the plate completely and satisfactorily with the gelatine mixture, but even if the plate is covered to within 0·5 in. of its edges with a satisfactory layer the experiment may proceed. The plate is next lowered on to the horizontal surface and allowed to stand, at room temperature, for about 20 minutes so that the gel may properly set. The plate is then removed to a room which can be darkened, and placed on a horizontal support in a position such that it may later remain undisturbed. 5 small drops (each about 0·1 ml.) of a 25 per cent silver nitrate solution are now allowed to fall gently, from a fine burette-jet, on to the same position at the centre of the plate. As a result, a large drop of circular outline is formed at the chosen position. The room is then darkened, and the system allowed to stand for about 2 days, the plate being occasionally examined in diffused daylight. At the end of this period, any traces of the drop which still remain may be removed by means of a pointed strip of filter-paper, the gel being then allowed to dry. Concentric bands of precipitate will be observed. They may be preserved in a dry place.

The procedure just outlined may, in the production of silver chromate rings, be modified by placing enough of a potassium chromate-gelatine mixture (0·1 gram potassium chromate, 4 grams of gelatine, 100 ml. of hot water) in a test tube to fill the tube to about two-thirds of its capacity, and allowing the gel to set. A few ml. of 8 per cent silver nitrate is then poured on top of the gel, and the tube set aside in darkness for some hours. Bands of silver chromate develop in the system, but the banding may not be as sharp as in the previous case.

Copper Chromate Bands. Holmes[1] gives the following method of producing copper chromate bands, which bands are very distinct: A mixture of water-glass (sp. gr. 1·06) and 0·5 N acetic acid in a test tube is made 0·1 N with respect to potassium chromate, and allowed to gel. The gel is later covered with 0·5 N copper sulphate solution. After about 2 days of standing, bands are formed.

Lead Iodide Bands. Prepare, and filter through cotton-wool, 100 ml. of a 1 per cent agar sol, and in it dissolve 4 grams of potassium iodide. Two-thirds fill a test tube with hot mixture, and allow the test tube and contents to cool slowly. When room temperature is reached, pour on the gel a few ml. of a 30 per cent solution of pure lead nitrate. On standing, the ring-formation will develop in the system relatively rapidly.

Gold Bands. Holmes' method for the preparation of gold bands was as follows: Equal volumes of water-glass (sp. gr. 1·16) and 3 N sulphuric acid were mixed. To 25 ml. of the mixture 1 ml. of 1 per cent gold chloride was added. When the solid gel had formed (after 1 or 2 days) it was covered with a saturated solution (about 8 per cent) of oxalic acid (reducing agent). A beautiful series of 'rainbow-coloured' bands of colloidal gold developed, with golden crystals scattered throughout the gel.

Davies showed that light of short wave-length has considerable influence on the formation of colloidal gold in such gels.

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[1] Alexander's *Colloid Chemistry,* 1926; Holmes' *Laboratory Manual of Colloid Chemistry,* 1928.

SECTION 3: MEASUREMENT

A number of the physico-chemical methods followed in the study of colloid systems are described under the separate headings 'Ultramicroscopy', 'Ultrafiltration', 'The Ultracentrifuge', 'Diffusion', 'Dialysis', 'Adsorption', 'Measurement of Film-thickness (Film-Balance)', 'Viscometry', 'Surface Tension', 'Nephelometry', 'The Electron Microscope', &c. Some other methods also are given in this section.

'Gold Number' Determination. **Zsigmondy's Technique.** 0·01 ml. of the protective colloid sol is placed in a small clean beaker, 0·10 ml. in a second beaker, and 1·00 ml. in a third beaker. 10 ml. of the standard gold sol is added to each beaker, and the mixtures are vigorously shaken for 3 minutes (this interval is usually considered sufficient for adsorption to take place). 1 ml. of 10 per cent sodium chloride solution is next run in to each beaker, with simultaneous stirring. The beakers should then be examined by pure transmitted light (e.g. by looking through the system towards a uniformly illuminated white screen). Suppose the colour-change occurs in the first beaker, but not in the others, then the gold number lies between the values represented by the masses of protective colloid in 0·01 ml. and 0·10 ml. of the protective colloid sol. For a more exact determination the procedure is repeated using volumes in the narrower range 0·01–0·10 ml. Finally, the number of milligrams of the protective colloid which just fails to prevent the colour-change is given as the gold number.

Hatschek preferred to express the final answer as the minimum concentration in per cent which just prevents the colour-change. Thus, if the addition of 0·2 ml. of the emulsoid sol to 10 ml. of the gold sol just prevents the colour-change on the addition of the sodium chloride, the gold number in percentage would be

$$\frac{2}{102} \times \text{(original emulsoid concentration)}$$

Determination of Isoelectric Point. When an ampholyte is fairly soluble, one method of determination of its isoelectric point is based on the fact that equal numbers of anions and cations are yielded by the ampholyte at the point in question. A series of dilute buffer solutions of graded *p*H-values is prepared Portions of the ampholyte are added to the different buffer solutions, the buffer which suffers no consequential change in *p*H will have the *p*H-value of the isoelectric point. The ampholyte will change the *p*H of the other buffers, behaving as a base towards buffers of low *p*H-value (thus tending to raise the *p*H), and as an acid towards buffers of high *p*H-value (thus tending to lower the *p*H).

Another method of finding the isoelectric point consists in determining the *p*H corresponding to minimum solubility. The solubility of genuine proteins in water is minimum at or near the isoelectric point and increases, usually, when an acid or an alkali is added, since ionised protein salts (and amphoteric electrolytes in general) are more soluble in water than the unionized molecules. Since proteins are least ionized at the isoelectric point, their solubility, at this point, is also minimum. This method has been employed [1] in the cases of certain amino acids of low solubility. Adequate equal portions of the ampholyte are added to a series of heated buffers of equal volumes. The solutions are then allowed to cool, and the quantities of crystals which separate are compared. The *p*H-value corresponding to minimum solubility may thus be found. It sometimes happens that a 'range' of minimum solubility is encountered, corresponding to an isoelectric 'range' rather than an isoelectric 'point'.

Measurement of Rate of Coagulation. For the measurement of the rate of coagulation of a sol, the counting of the number of particles per given volume of the sol, by the aid of the ultramicroscope, at intervals during the process of the coagulation, would be a direct, and, under certain circumstances, an accurate method of experimentation. There are, however, practical difficulties inherent in the method, and it applies only in those cases where the sols are *completely* resolvable by the use of the ultramicroscope.

Hatschek [2] described a simple apparatus involving the use of two wedge-shaped compartments in a cell for the investigation of the velocity of coagulation of a gold sol.

Wo. Ostwald and von Hahn [3] described a 'Kinetic Flocculation Meter' which operates on the principle of the change in level of the sol in one arm of a special U-tube according as the density of the sol changes due to coalescence and sedimentation of the dispersed particles.

Some simpler indirect methods have been applied, e.g. variation of surface tension, of viscosity, or of turbidity with time.

Comparison [4] of Liminal Values of Electrolytes in respect of a given Hydrosol. 5-ml. samples of the hydrosol are added to each of a series of well-cleaned test tubes. Solutions of various electrolytes, of various concentrations, are taken, and 5-ml. portions of the different electrolyte solutions are then added, each to its own sol sample, the mixing in each case being effected by rapid pouring-in of the electrolyte, pouring back into the empty test tube, and finally re-pouring into the original test tube. The mixtures are set aside for a period of about 2 hours (or alternatively centrifuged for 2 minutes) and then examined for extent of precipitation. Suppose, in the case of a given electrolyte, that precipitation is judged to be complete (as evidenced by the clear supernatant liquid) at an electrolyte concentration (in the mixture of sol and electrolyte) of C_1, and is not complete at the next lowest concentration C_2, then the mean of the concentrations C_1 and C_2 is taken to be the 'precipitation concentration' ('liminal value', 'liminal concentration').

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[1] Michaelis and Davidsohn, *Biochem. Z.*, 1911, *30*, 143.

[2] *Laboratory Manual of Elementary Colloid Chemistry* (Churchill, 1925).

[3] *Kolloid-Z.*, 1922, *30*, 62.

[4] *See* Freundlich, *Z. physik. Chem.*, 1903, *44*, 129.

Setting-points and Melting-points of Gels. Hatschek[1] suggested the apparatus illustrated in Figs. 23 and 24 (XV^3) for the determination of the melting-points and setting-points of gels. The test tube T (about 6 in. × ⅝ in.) is suspended in the centre of a beaker B of about 400 ml. capacity (which beaker acts as a water-bath) by means of the guide G (Fig. 24 (XV^3)) through which the test tube will freely slide. T is weighted with about 20 grams of mercury, and should be perpendicular when resting on G ; if the rim is not regular, a square collar (e.g. of rubber) should be used and permanently attached to the tube. The glass rod R (about ⅜ in. in diameter) is suspended with its axis exactly coinciding with the axis of T. H is a thermometer. In operation, the beaker at first contains cold water at (say) 15°, and a definite volume of the sol (e.g. a gelatine sol) is placed in the test tube. The sol is then allowed to set to a gel for a definite time. The rod, with the test tube and contents hanging to it, is now raised to a definite height, and the temperature of the bath is raised slowly and with constant stirring. At a certain temperature the test tube will slide off the cylinder of gel which surrounds the rod, and will come to rest on G (Fig. 24 (XV^3)). The temperature at this instant is recorded as the melting-point.

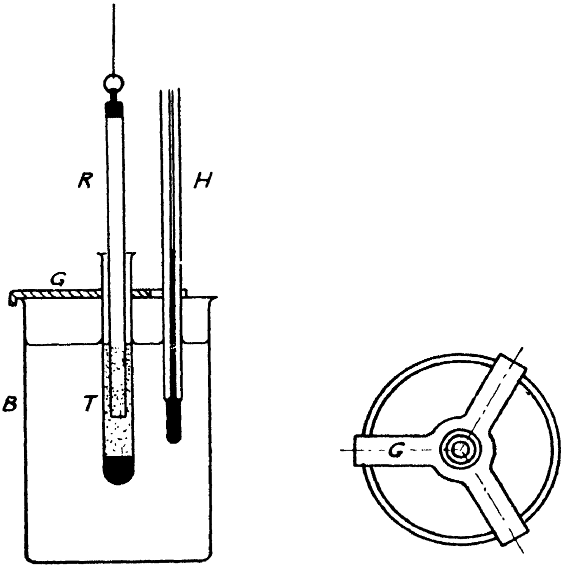

FIG. 23 (XV^3)　FIG. 24 (XV^3)

Apparatus for determining melting-points and setting-points of gels—plan and elevation

To determine the setting-point. The rod is lowered to its original position, and the bath allowed to cool spontaneously. The rod is very slightly raised occasionally until a temperature is reached at which it just lifts the test tube. This temperature is taken as the setting-point. It should be remembered that the temperature of the sol-gel transformation and that of the gel-sol transformation depend on the 'rate of cooling' and 'rate of heating' respectively. Accordingly, in a series of experiments where results are to be compared, the cooling or heating should be carried out at a fixed rate, e.g. 1 degree per minute (before the transformation sets in); this rate may be regarded as the 'normal' rate (a rate of 1 degree per 5 minutes, sometimes desirable, would be a 0·2 normal rate).

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[1] *Laboratory Manual of Elementary Colloid Chemistry* (London, 1925).

'Time of Setting' of a Gel. The 'time of setting' of a gel may be determined for comparative purposes by finding the time-interval which must elapse before some arbitrarily chosen condition of mechanical rigidity is assumed by the system. One method of determination consists in noting the minimum time which must elapse in order that flow of the system may not take place when a cylindrical tube, of a selected diameter, containing the system is inverted. Another method consists in measuring the time which must elapse before a condition obtains in which a sphere, of chosen diameter and density, is prevented from falling through the system.

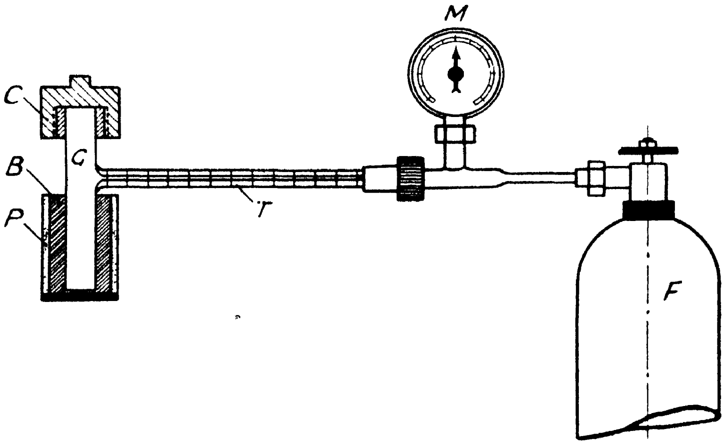

FIG. 25 (XV^{3})
Posnjak's apparatus (schematic)

Swelling. One method of investigating the phenomenon of swelling is due to Posnjak.[1] The apparatus is indicated schematically in Fig. 25 (XV^{3}). The glass tube G was attached to the porous pot P by means of the cement B. The tube was closed by the cap C, and was connected to a side-tube consisting of a graduated capillary T through which pressure could be exerted on the contents of G by means of the gas compressed in the cylinder F. The pressure was determined on the manometer M.

In an investigation on the swelling of Para rubber for different organic media, a small disk of the rubber was introduced through the tube D, so that it lay on the porous bottom. Mercury was then poured into the tube so that the tube was completely filled and the capillary T partly filled. The porous pot was then placed in a beaker containing the organic liquid. As the rubber disk swelled, due to entry of the organic liquid through the porous pot, the swelling was recorded by noting the displacement of the mercury in the capillary, and the gas-pressure necessary to prevent movement of the mercury was also read. In this manner the pressures corresponding to different degrees of swelling were determined. Fig. 26 (XV³) illustrates some of Posnjak's results, the particular organic media being as indicated. Freundlich pointed out that for such curves the empirical equation

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[1] *Kolloidchem. Beihefte*, 1912, *3*, 417.

$$\log p = \log p_1 + k \log c$$

applies, where p = pressure of swelling; c = concentration of rubber in the swollen gel; p_1 is the value of p when $c = 1$; k is substantially a constant.

In the plastics industry the extents of (limited) swelling on immersion in water and of water-absorption of a material are measured as follows: A disc, 50 mm. in diameter and 12 mm. thick, is moulded from the moulding-powder, which may be of the thermo-plastic or thermo-setting variety. Material of 0·5 mm. thickness is then removed from all surfaces of the moulding by careful machining. The faces of the specimen are then smoothly finished by means of fine sandpaper until the disc has a diameter 48 mm. ± 0·2 and a thickness of 10 mm. ± 0·2. The disc is now air-dried for 1 hour at 50° C., cooled and accurately weighed. It is then measured across a marked diameter and the thickness measured at two marked positions. The disc is then immersed in water at 15° to 25° C. for a period of 7 complete days, removed, surface-water removed thoroughly by means of filter-paper, allowed to stand in air for 5 minutes, then re-weighed and re-measured at the marked places. Percentage water-absorption and percentage swelling due to immersion are then calculated.

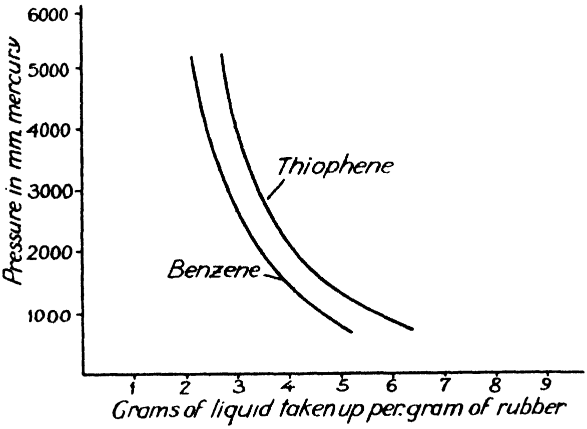

FIG. 26 (XV³)
Some 'swelling-pressure' curves (Posnjak)

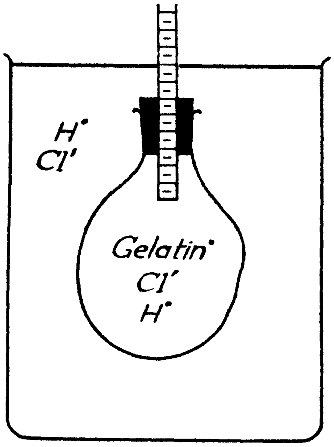

FIG. 27 (XV³)
Experiment of Loeb and Michaelis

Application of the Donnan Equilibrium. Fig. 27 (XV³) illustrates an experiment due to Loeb and Michaelis. It represents a collodion sac of capacity about 50 ml., fitted with a bored rubber stopper which is cemented to the sac by means of collodion solution and bound on by a wide rubber band. The sac holds a solution of originally isoelectric gelatine of concentration 1 gram (dry weight) in 100 ml. of N/2,000 hydrochloric acid, and through the stopper passes a very coarse capillary tube of length about

25 cm. The arrangement is immersed, as shown, in 350 ml. of N/2,000 hydrochloric acid contained in a suitable beaker. If the system be kept at 24° C. for 6 hours, osmotic equilibrium will be reached. The osmotic pressure may then be read. The capillary manometer is then replaced by a funnel, and some of the solution may be forced into the funnel by pressing the sac against the side of the beaker. After 20 hours (or longer) potassium chloride agar tubes, dipping into the inner and outer solutions and connected with saturated calomel electrodes, may be used to determine the potential difference (0·017 volt, with the inner solution positive). The pH-values of the inner and outer solutions may also be determined,[1] and the potential difference calculated treating the arrangement as a hydrogen-ion concentration cell. The error is small.

One scheme for finding the potential difference between the inner protein solution and the outer aqueous solution (i.e. the so-called 'membrane potential') consists of the use of a Compton electrometer associated with two potassium chloride-calomel electrodes arranged as follows:

Hg	Hg_2Cl_2	Saturated KCl solution	Gelatine-acid solution	Collodion sac	Outer aqueous solution	Saturated KCl solution	Hg_2Cl_2	Hg

The e.m.f. of this cell is then determined.

Dialysis (*see* Vol. II, Chap. V).

An Apparatus for Low-temperature Dialysis. Both speed and low temperatures are highly desirable in the dialysis of sensitive protein solutions. When small refrigerators are used instead of cold rooms, the apparatus used to increase the velocity of dialysis has to be sacrificed to space requirements. For example, the Kunitz[2] dialyser, in which a stream of pure water is allowed to flow over a rocking dialysis sac containing a marble, cannot be set up in an ordinary laboratory refrigerator.

If a dialysis sac containing a salt solution is suspended in water, the greater density of the solution dialysing out causes it to flow downwards, and currents can be seen streaming away from the bottom of the sac. In the dialyser of Falconer and Taylor [3] an attempt has been made to utilize this fact to set up a circulation which results in a constant supply of fresh water to the outside of the dialysis sac. The apparatus (Fig. 28 (XV^3)) consists of a tall dialysis vessel A of about 7·5 cm. diameter by 40 cm. high containing a second flow-directing vessel B about 15 cm. total

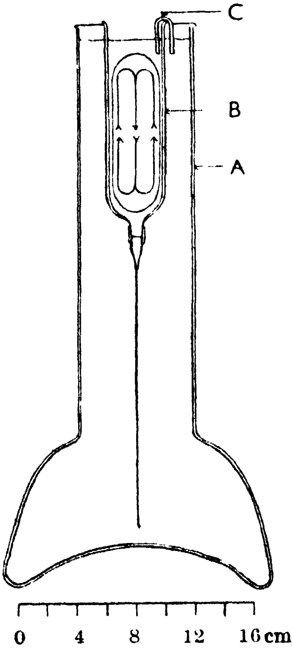

FIG. 28 (XV^3)
Dialyser of Falconer and Taylor

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[1] E.g. By means of a hydrogen electrode.

[2] Kunitz and Simms, *J. Gen. Physiol.*, 1928, *11*, 641.

[3] *Nature*, 1944, *154*, 87. This account from *Nature* is published with the permission of the authors. The electro is supplied by the Editor of *Nature*.

length by 3·5 cm. in diameter ending in a jet. The dialysis sac is placed in the inner vessel, and the water in the inside and outside vessels connected by a syphon C of approximately 2 mm. bore.

The flow of the denser salt-containing fluid out through the jet can be easily followed either by direct observation or by placing a flash-lamp bulb on one side of the vessel about 1 ft. away and a sheet of paper on the other side at a similar distance, when a Schlieren picture of the stream will be projected on to the paper. The fine stream of fluid from the jet passes almost to the bottom of vessel A without breaking up, and even after it has broken up the fragments continue on their way downwards. This flow results in the dense salt solution collecting at the bottom of vessel A, while fresh water is being continuously supplied around the dialysis sac. The process lasts for 24–48 hours, depending on the initial volume and concentration of the dialysing fluid, and continues until the salt solution has risen to the level of the jet.

Simultaneously, another circulation is taking place inside the sac. It can be observed by watching the movement of small particles of dust, &c., just inside the membrane, where the fluid, owing to loss of salt, rises slowly, while that in the centre of the sac falls, resulting not only in mixing inside the sac but also in the maximum differential salt concentration being developed across the membrane due to the counter-current principle. The flow of fluid inside and outside the membrane also helps to abolish skin effects which restrict diffusion due to stagnant surface layers.

The dimensions of the apparatus, especially height of vessel A and jet size, play an important part in efficiency. We have not observed unbroken flow streams of more than 20 cm. from jets used, and it therefore seems that no great increase in efficiency would result from making the apparatus any taller. The optimum diameter of the jet appears to be about 0·4 mm.

The dialysis time for a 0·5 saturated ammonium sulphate solution under these conditions is about 30 hours, and the final concentration inside the sac is approximately 1/500 of the initial concentration, that is, of the order of 0·1 mgm. nitrogen/ml. This dilution corresponds to 1/12 of the concentration that would occur if all the salt in the sac were to be evenly distributed throughout the whole volume of the dialysate.

To avoid salt contamination of the water in the outside vessel, the apparatus is set up as follows. The dialysis sac is placed inside vessel B, and B is then lowered into A, which already contains the approximately correct volume of water. When the inside and outside levels are the same, the syphon is filled and dropped into place.

Dialysis Membrane. Seamless cellophane tube is by far the best for this purpose.[1]

Filling and tying off the Dialysis Sac. (1) The cellophane is soaked in water for a few minutes.

(2) One end is folded five times thus, it is then twisted and an ordinary knot tied.

(3) The solution to be dialysed is next put in, surplus air gently squeezed out and the cellophane tube above the liquid twisted. It is advisable at

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[1] Supplies are obtainable from the Visting Corporation, U.S.A., whose British agents are John Crampton & Co. Ltd., Pomona Spice House, Wythenshawe, Manchester.

this stage to squeeze the tube to stretch the cellophane and to test for leaks. The dialysis sac is now tied off above the fluid with soft 20-strand cotton twine. Ordinary hard twine sometimes cuts the cellophane.

The Ultra-microscope (*see* Vol. II).

Micellar Weight by Sedimentation-equilibrium Method. Svedberg and Fåhraeus [1] used the ultracentrifuge in the determination of the molecular weight of haemoglobin. The ultracentrifuge used was previously described.[2] From 0·01 ml. to 0·25 ml. of the solution studied was enclosed in a cell of glass or quartz, the walls of which were plane and parallel. The arrangement was rotated at a steady temperature in a centrifuge so arranged as to allow the photographing of the solution at various intervals on its way to sedimentation-equilibrium and after the equilibrium had been reached, while the centrifugal force acting had a value up to 5,000 times as large as the force of gravity. When the equilibrium was reached and the cell contents photographed, a series of solutions of different concentrations was photographed (using in each case the same cell as previously) shortly after the commencement of centrifuging, i.e. before any marked sedimentation had set in. The plate carrying the photograph of the solution on its way to equilibrium and after reaching it, as well as the scale of solutions of different concentrations, was then recorded by the use of a self-registering micro-photometer. From such records the curves giving the relationship between the concentration of the solution and the distance from the centre of rotation were readily constructed. Fig. 29 (XV^3) shows curves obtained from the micro-photometric records, illustrating the progress of the centrifuging of a 2 per cent solution of carbon monoxide-haemoglobin, the column of solution being 0·8 cm. long, and the rate of centrifuging 10,240 r.p.m. The abscissae represent the distances from the centre of rotation, and the ordinates are the deflections of the galvanometer which was associated with the micro-photometer. Any observed deflection was substantially proportional to the corresponding

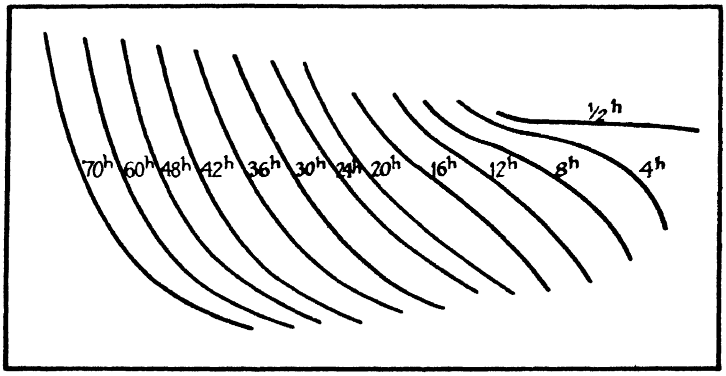

FIG. 29 (XV^3)

Curves based on micro-photometric records concentration of the solution. The curves are successively displaced by regular intervals to the left to avoid confusion. The cells used were constructed as follows : Each cell was made up of three circular glass or quartz plates 2·0 cm. in diameter, cemented together with de Khotinsky cement and surrounded by a brass ring as illustrated in Fig. 30 (XV^3). From the middle plate had been cut a sectorial aperture of 5° angle and 5·2 cm. equivalent radius. This aperture formed the cavity in which the solution was to be placed. In most of the experiments the thickness of the layer of solution was 0·145 cm., but in some cases it was 0·98 cm. The method employed to prevent evaporation (and consequent effects) was to cover the solution with a layer of liquid paraffin. The cell-holder was a brass ring which took two pairs of cells of different thickness, as illustrated in Fig. 31 (XV^3). Two ring-shaped brass plates (not illustrated) of the same outline as the cell-holder and provided with four sectorial apertures were screwed to the cell-holder, clamping the cells together firmly. An ebonite plate provided with only one sectorial aperture cut out all the light except that from the chosen cell.

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[1] *J. Amer. Chem. Soc.*, 1926, *48*, 430.

[2] Svedberg and Rinde, *ibid.*, 1924, *46*, 2677.

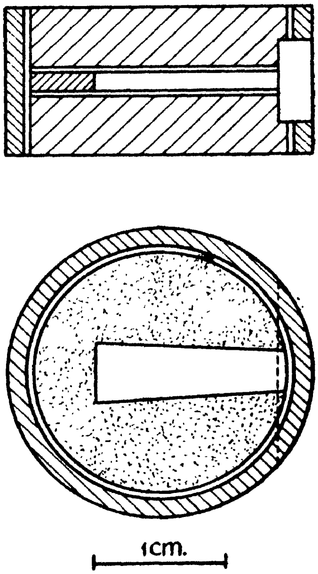

FIG. 30 (XV^3)
Construction of special cell

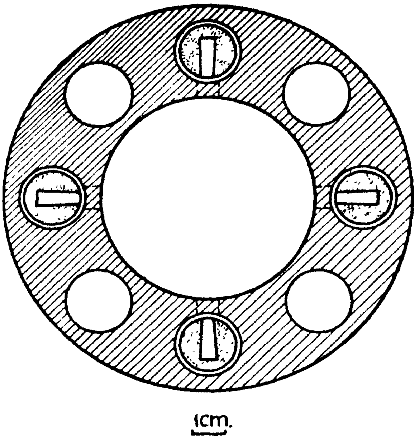

FIG. 31 (XV^3
Cell-holder

The time of centrifuging necessary for the reaching of the sedimentation-equilibrium was found to be about 6 hours per 0·1 cm. length of solution-column in the cases investigated, so that the 0·5-cm. length of column usually chosen required 30 hours of centrifuge-treatment. The magnification of the micro-photometer was 10, and the photographs of the column were taken in the scale 1 : 1, so that an abscissa of 0·1 cm. in the photograph corresponded to 1·0 cm. in the micro-photometric curve. In the calculation of the molecular weight from the sedimentation-equilibrium curve giving the relationship between concentration and distance from the centre of rotation, employing the equation (13) already given in Section 1, viz.

$$M = \frac{2RT \log_e \frac{C_2}{C_1}}{\omega^2(1 - Vd_2)(x_2{}^2 - x_1{}^2)}$$

$(x_2 - x_1)$ was taken equal to 0·05 cm. Thus by using a solution column-length of 0·5 cm., ten separate computations were possible. Assuming all the solute-molecules (micelles) to be of equal mass, the answers should all correspond. If the molecules, due to partial association, had different masses, the values of the molecular weights should decrease from the base of the cell upwards.

In the study of proteins which absorb in the visible spectrum, a suitable incandescent lamp eventually combined with light-filters was used as source of light. This lamp was fed by accumulators and the voltage was carefully controlled. Where the proteins absorb only in the ultra-violet region, a quartz mercury lamp with filters of gaseous chlorine and bromine was recommended, the optical parts of the centrifuge being, in such a case, made of quartz or flourite. For a method of determining the molecular weight of highly polymerized substances by a process based on the Staudinger viscosity equations, *see*, for example, Kemp and Peters.[1]

Electrophoretic Mobility (*see also* Section on 'Emulsions'). **Transference (Transport) Method of Measuring.** One method of determining the value of electrophoretic mobility by transference is that due to Paine.[2] Fig. 32 (XV[3]) shows the modification of Paine's apparatus used by Henry and Brittain,[3] in experiments on a silver sol. All vessels in which the sol was contained were made of Pyrex or Jena normal glass, and were rigorously cleansed by treatment with chromic acid, followed by steaming or washing in distilled water. Attention to this matter was found to be absolutely necessary if the current which was to pass through the system were to remain tolerably constant.

The inverted U-tube had a length of 65 cm., an internal diameter of 1·5 cm., and a capacity of 105 ml. The electrode-vessels into which the U-tube was inserted were close-fitting so that the volume of the sol needed for the experiment could be limited to 200 ml., thus increasing the relative precision of the analytical determinations. The main electrodes, by means of which current was admitted to the system, consisted of strips of platinum foil, each 1 cm. wide, wrapped tightly around the outside and near the extremities of the U-tube. In this way any products of electrolysis, irrespective of density, were mainly confined to the electrode-vessels. Current was drawn from a 200-volt D.C. mains through variable resistances. A was a micro-ammeter used to measure the total current flowing. Subsidiary electrodes, consisting of platinum points sealed through the bend of the U-tube at a distance apart of about 4 cm., were used to control the potential gradient in the sol column, and were connected to a potentiometer system as illustrated. P was the potentiometer (of dial pattern), GS a shunted galvanometer, and V a high-resistance voltmeter by means of which the potential difference at balance could be read.

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[1] *Ind. and Eng. Chem.* (*Ind.*), 1941, *33*, 1263.
[2] *Trans. Farad. Soc.*, 1928, *24*, 412.
[3] *Ibid.*, 1933, *29*, 798.

The U-tube was filled by suction, and a current of a few tenths of a milliampere passed for a period of about 2 hours. The tap was then opened and the sol allowed to fall back into the electrode vessels. The temperature of the system was maintained throughout in an air thermostat at 25° ± 0·5 degree. The silver in each vessel, including any which had adhered to the main electrodes, was then brought into solution with a little nitric acid, and the liquids from the vessels each evaporated to about 25 ml. The silver-contents were then determined by means of N/100 ammonium thiocyanate, run in from a calibrated micro-burette, using ferric alum as indicator.

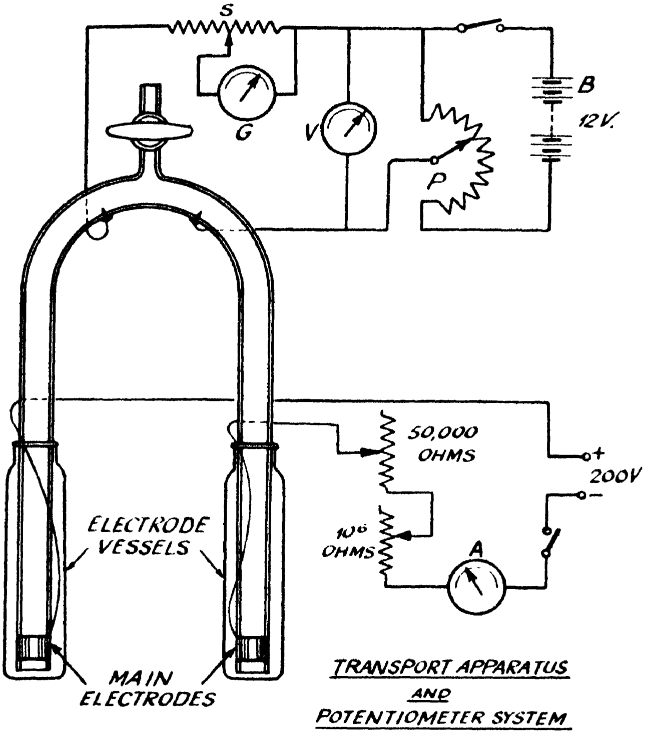

FIG. 32 (XV^a)
Electrophoretic mobility measurement

The mobility, u, of the colloidal micelle, was found from the equation:

$$u = \frac{m\kappa}{Mit} = \frac{mD}{MVt} \quad . \quad . \quad . \quad . \quad (33\alpha, 33\beta)$$

where m = mass of colloid transported from the cathode to the anode compartment

M = mass of colloid per ml. of the original sol

κ = specific conductance of the sol at the point where separation into two parts took place, i.e. at the top of the bend

t = time of electrolysis in seconds
it = number of coulombs which passed
V = potential difference (assumed constant) between two points in the liquid column not subject to disturbance by the products of electrolysis
D = a constant, which depended on the form of the apparatus and the position of the points to which reference has just been made. This constant could be determined by calibration with an electrolyte of known specific conductance.

In the course of the experiments, the authors maintained V, as measured between the subsidiary electrodes, at a constant value by increasing the external resistance from time to time. The current, i, remained constant during the greater part of each run, but showed a small increase in the initial, and sometimes in the final stages. This value of V was then inserted in equation (33β) to determine the mobility. It was also possible, by using equation (33β) to obtain values for the mobility, but there existed some discrepancy between the values as calculated from (33 α) and those calculated from (33β). The cause of this discrepancy was uncertain. Lest polarization-effects had caused errors in the value of V, the values of the mobility calculated by means of (33α) were taken to be more reliable. The specific conductance of the sol was determined on the Wheatstone net principle, using audio-frequency current from a valve oscillator together with a correctly designed conductivity cell and the usual devices for balancing cell-capacity. If the final rise in current intensity were due to contamination it was held that the effect would have been of short duration and, in any case, it was small. Temperature disturbances were held to be relatively small, and diffusion effects to be inoperative, and the opinion was formed that results calculated by the use of (33α) probably represented the true values of the mobility of the micelles with an uncertainty of from 3 to 4 per cent, the greater part of which uncertainty was due to analytical difficulties.

NOTE. *Distinction between Nernst and ζ-Potentials* (*see* p. 367).

More correctly the Nernst potential is the total fall in potential between the *interior* of the solid and the interior of the liquid. The fall of potential between the interior of the solid and the solid wall, W, may be considerable, e.g. of the order 100 millivolts as compared with $(\varepsilon_W - \varepsilon_F)$ of the order 10 millivolts and $(\varepsilon_F - \varepsilon_1)$ of the order 70 millivolts.

CHAPTER XVI[3]

EMULSIONS

SECTION 1: THE NATURE OF EMULSIONS

Emulsion Types

AN ordinary emulsion is a system containing two 'immiscible' (or nearly immiscible) liquids, one liquid (the 'external phase') being continuous, and in it the other liquid (the 'internal' or 'disperse' phase) is dispersed in the form of globules or droplets. Oil dispersed as droplets in water would give a system which is termed as oil-in-water, or O/W emulsion. Water dispersed in oil would constitute a water-in-oil, or W/O, emulsion. In this connexion, an 'oil' generally means a liquid which is immiscible with water. The use of the terms 'obverse' and 'reverse' to describe O/W and W/O emulsions respectively has been suggested.[1]

Broadly considered, two distinct categories of emulsions are recognized, viz.:

(*a*) The 'Oil Hydrosols' (produced by methods indicated later. *See* Preparation of Emulsions). These are very dilute O/W emulsions. The term 'hydrosol' originates from analogy with suspensoid sols. The analogy arises mainly through the fact that such emulsions are, like suspensoid sols, stable in dilute 'solution' only, and that, in such cases, water is almost invariably the continuous phase. The stability of these emulsions is mainly associated with electrostatic charges on the droplets of the dispersed phase. The charge on each droplet, in the case where a pure oil is dispersed in pure water, is a negative one, and is thought to be due to the preferential adsorption, by the oil, of hydroxyl-ions from the water, the balancing positive ions forming another layer on the water side. Such a two-layer system is known as an 'electrical double-layer'.

'Condensed steam' from engines frequently consists of an oil hydrosol, containing about 1 part of oil to 10,000 parts of the liquid. This emulsion, being stable ('obstinate'), is a source of boiler inefficiency, and even of danger, if re-fed into the boiler. In such a case the oil droplets would have diameters considerably less than 1μ. Coalescence of the globules is impeded by mutual repulsion due to negative charges upon them.

(*N.B.* $1\mu = 1$ micron $= 0{\cdot}001$ mm. In literature, particularly on the medical side, μ (the micron) has often been misnamed 'the micromillimetre'. Some confusion has therefore resulted. The micromillimetre $(\mu\mu) = 10^{-6}$ mm.)

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[1] *J. Soc. Chem. Ind.*, 1943, *62*, 123.

(*b*) Emulsions in which permanency is achieved through the use, in the process of the making of the emulsion, of an emulsifying agent. There are a number of theories as to the manner in which emulsifying agents act, but the idea of protective, resistant, non-adhesive films of the agent around the globules is well established.

Thus, emulsions of the (*a*) class are two-component, two-phase systems, while those of the (*b*) class may be considered as three-component, three-phase systems. Emulsions of the (*b*) class are far more important, from a practical point of view, than those of the (*a*) category.

A third (but rather uncommon) category may be mentioned, i.e. emulsions stabilized by ordinary electrolytes such as inorganic bromides or thiocyanates.[1]

Emulsifying Agent (Emulsifier,[2] Stabilizer,[3] Emulgent). This may be regarded as a ‘ foreign ’ substance which, when present in a liquid-liquid system, sponsors the preparation of a permanent emulsion. The relative amount of this third substance present in the system is usually small, e.g. 1 per cent calculated on the continuous phase. In technical practice it is customary to employ a mixture of emulsifying agents for optimum effect. Thus one agent might promote fine emulsions with poor viscosity, while another might promote coarse emulsions with high viscosity. A suitable mixture of these agents might be used to produce an emulsion of reasonable viscosity containing the internal phase in a suitable degree of fineness.

Cases are known in which the globules of the internal phase contain, within themselves, smaller droplets of the primary ‘ continuous ’ phase and these droplets, in turn, contain still smaller globules of the original ‘ internal ’ phase, and so on. Such multiple emulsions may sometimes be obtained by the simultaneous use of antagonistic emulsifying agents (*see later*), for instance, a mixture of a magnesium soap and a sodium soap. The term ‘ antagonistic ’ is the one commonly used to indicate that some of the agents under consideration will sponsor the O/W type of emulsion, while the others will promote the W/O type. Multiple emulsions often arise as a result of the phenomenon of phase-inversion.

Although many emulsifying agents, very effective in specific cases, are known, not one approaches in its characteristics the qualities of an ‘ ideal ’ agent. The attributes necessary for classification as an ideal agent would be manifold, one requirement being that such an agent should be universally effective for the production of emulsions of a given type (e.g. O/W). Soaps (e.g. metallic oleates), other colloids, sulphonated organic compounds, hydroxy-amines, and finely divided solids, are examples of the many types of substance which are employed as emulsifying agents. Potassium soaps are usually somewhat more effective than the corresponding sodium soaps. Hydrophilic colloids tend to promote O/W emulsions; olephilic colloids usually sponsor W/O emulsions. Bancroft illustrated a simple formulation due to Briggs by stating that if the emulsifying agent is a water-soluble colloid, and is adsorbed strongly at the interface, but is not peptized to a marked extent by the oil (i.e. is mainly lying in the water phase), an O/W emulsion will result. Conversely, an oil-soluble colloid, well adsorbed at the interface, but not well peptized by water, will favour W/O emulsions. There are, however, some agents which appear to behave exceptionally in this respect. McBain and O'Connor [1] have shown that certain hydrocarbons, normally insoluble in water, actually dissolve to some extent in dilute potassium oleate solution, and to an even greater extent in soap solutions containing small additions of sodium silicate or caustic potash. The colloidal solutions formed are thermodynamically stable, because the vapour-pressure is considerably less than that exhibited by the pure hydrocarbon at the same temperature until a point is reached when the solution becomes approximately saturated. It is only when excess above this is added that there is any real emulsion.

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[1] Cheesman and King, *Trans. Farad. Soc.*, 1940, *36*, 241.

[2] The term ‘ emulsifier ’ is sometimes applied to emulsifying machines.

[3] The term ‘ stabilizer ’ is sometimes restricted to describe those substances which help to increase the stability or the permanence of an emulsion-system.

The 'Surface Tension Theory' of emulsification, advocated by Quinke and by Donnan and Potts, states that any substance which lowers surface tension, and which is accordingly adsorbed at the interface, will tend to promote emulsification.

Bancroft held that the type of emulsion formed depends on the relative interfacial tensions on the two sides of the adsorbed film or membrane, the liquid having the lower interfacial tension, relatively to the film, becoming the continuous phase.

The term 'hydrotropic' has been applied to crystalloidal and colloidal emulsifying agents. When certain hydrosols are used as emulsifying agents, it may be necessary to add mild flocculating agents to force the colloidal substance, in the condition of a fine solid, to the interface. Thus, a ferric oxide hydrosol, which failed to emulsify benzene in water, was found by Briggs to be effective when sodium chloride was added in certain concentrations. Briggs held that if such an emulsifying agent is peptized too well by the continuous phase, no adsorption-film will be formed.

Schulman and Cockbain have deduced that for the formation of satisfactory stable emulsions it is necessary to have at the surface of the globule a composite film consisting of at least two components. One of these components should be water-soluble and should come from the aqueous phase, the other component should come from the oil phase. These two agents should have suitable shapes and suitable attractive forces to ensure film-stability, and the composite film must greatly reduce interfacial tension. The film should be in the condensed liquid condition, which would ensure a maximum concentration of the agents at the interface and, at the same time, give the film the flexibility necessary to withstand transient distortions of the droplet. Any electrical charges necessary for stability would be provided by the ions of that agent which came from the aqueous phase. These ions would be held in position within the composite film in such a way that they would be unable to repel each other.

It is held that a solid emulsifying agent, to be effective, must be capable of being wetted, though not equally, by both liquids (*see* under Wetting). Clowes incorporated into Bancroft's 'relative surface tensions' Theory

[1] *J. Amer. Chem. Soc.*, 1940, *62*, 2855.

(*see above*) the idea that the liquid which better wets the emulsifying agent becomes the continuous phase.

The use of oil-in-water emulsions, in which the emulsifying agent is 'cation-active' (i.e. the hydrophilic head of the molecule is positively charged) or is 'anion-active' (i.e. the hydrophilic head is negatively charged, e.g. a soap of an alkali metal), has recently been suggested [1] for the reduction of dust-borne bacteria carried by textiles.

King and Mukherjee [2] found that emulsions stabilized by other hydrophilic colloids are, on the whole, 'coarser' but more 'stable' than corresponding soap-stabilized emulsions.

Phase-volume Concentration (i.e. the fraction of the total volume occupied by a given phase).

Mathematical treatment indicates that small, uniform spheres, when in the condition of closest packing—*see* Fig. 1 (XVI[3])—will occupy a maximum of 74·02 per cent, by volume, of the available space.

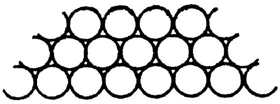

FIG. 1 (XVI[3])
Closest packing of uniform spheres

In practice, however, emulsions can be prepared in which the volume-concentration of the internal phase greatly exceeds this mathematical maximum. This has been attributed to the fact that the globules are not of uniform size,[3] neither are they all perfect spheres since the shapes may be distorted owing to the pressures exerted on them by neighbouring globules. Owing to the presence, on the surface of the globules, of films of the emulsifying agent, coalescence is retarded in such concentrated emulsions. The phase-volume concentration exercises a considerable influence on some of the characteristics, and often on the type, of the emulsion formed. One characteristic upon which it has a marked influence is that of viscosity.

Viscosity of Emulsion Systems

Einstein deduced a formula for the viscosity, η, of a system consisting of rigid spheres suspended in a given liquid, viz.

$$\eta_1 = \eta\,(1 + b\varphi),$$

where η = viscosity of the continuous liquid, in the pure conditions;
φ = phase-volume concentration of the spheres;
b = a numerical coefficient, to which Einstein gave the value 2·5.

Staudinger [4] called the quantity $\frac{\eta_1}{\eta} - 1$, $(= b\varphi)$, the 'specific viscosity', but this term has been criticized on the grounds that it is not proportional to viscosity. The expression is dimensionless.

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[1] *See*, for instance, *B.M.J.*, 1944, *1*, 615.

[2] *J. Soc. Chem. Ind.*, 1940, *59*, 185.

[3] *See*, for example, Pickering, *J. Chem. Soc.*, 1907, *91*, 2002.

[4] *Die Hochmolekularen Organischen Verbindungen*, Springer, Berlin, 1932.

Hatschek gave a formula for the viscosity coefficient of a system of two liquid phases, assuming that the phase-volume concentration of the discontinuous phase was greater than 50 per cent. The formula was:

$$\eta_1 = \frac{A^{\frac{1}{3}}}{A^{\frac{1}{3}} - 1} \cdot \eta$$

where $A = \frac{1}{\varphi}$; η_1 and η are the viscosity coefficients of the system and the continuous phase respectively; φ has the same significance as previously.

When $$\eta = 1, \quad \left(\frac{\eta_1}{\eta_1 - 1}\right)^3 = A.$$

Modifications of the Hatschek formula have been found satisfactory in certain cases. Thus the formula

$$\eta_1 = \frac{\left(\frac{A}{h}\right)^{\frac{1}{3}}}{\left(\frac{A}{h}\right)^{\frac{1}{3}} - 1} \cdot \eta$$

is found to apply to certain emulsion-systems, where h is a number (termed the 'hydration factor') the value of which is often 1·3–1·4.

Egner claimed that no formula is thoroughly satisfactory. Taylor, in an extension of the Einstein formula, gives, for emulsions,

$$\eta_1 = \eta\left\{1 + 2{\cdot}5\varphi\left(\frac{\eta_d + \frac{2}{5}\eta}{\eta_d + \eta}\right)\right\}$$

where η_d = viscosity of the dispersed liquid in the pure condition.

Richardson,[1] who measured viscosities with a Couette apparatus, operating at an arbitrarily chosen mean angular velocity, developed an equation

$$\log_e \frac{\eta_1}{\eta} = k\varphi$$

where k is a numerical coefficient. This equation is somewhat similar to one proposed by Arrhenius and Kendall, in 1913, in connexion with colloidal solutions, viz.

$$\log_e \frac{\eta_1}{\eta} = kc$$

where c represents a concentration.

The viscosity of bitumen emulsions was studied by Eilers.[2] This author showed that for volume-concentrations of the dispersed phase between 0·0 and 0·65, the sixth-power formula of Bredee and de Booys—viz.

$$\eta_r = [1 + \{2{\cdot}5C_v/6(1 - C_v)\}]^6$$

η_r being the relative viscosity and C_v being the volume-concentration of the dispersed phase—was useful. For higher concentrations, however, the values got from this equation were too low. An equation

$$\eta_r = [1 + \{2{\cdot}5\,C_v/2(1 - aC_v)\}]^2$$

was proposed where a is a numerical coefficient.

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[1] *Kolloid-Z.*, **1933**, *65*, **32.**

[2] *Ibid.*, **1941**, *97*, **313.**

The viscosity of an emulsion of a given concentration, made from a given oil and water, may sometimes depend on the emulsifying agent used.

Emulsion Type.

It is well established that two immiscible liquids, A and B, for similar relative phase-volume concentrations may give, according to treatment, an emulsion of the A/B type or an emulsion of the B/A type. Some emulsifying agents are of the ' dual ' type, i.e. they are capable of stabilizing the A/B type or the B/A type, according to circumstances.

It is found that a number of factors may have a distinct influence on the type of emulsion produced from two liquids. Thus (*a*) the chemical nature of an oil, (*b*) the nature of the agent, (*c*) the temperature of emulsification, (*d*) mode of making the emulsion, (*e*) presence of other added substances, may affect profoundly the type or the character of the emulsion finally obtained.[1]

Tartar and others discovered the influence of temperature and concentration of stabilizer on emulsion-type. The following is a brief indication of the experimental procedure followed, where the agent was a soap of an alkali metal (sodium, potassium) : 5 ml. of benzene was added to 5 ml. of the warm aqueous soap-solution contained in a bottle. The system was stoppered, cooled, shaken for 5 minutes, and then tested for type. The temperature was then raised by 2·5 degrees, the system kept at the new temperature for 20 minutes, again shaken, and again tested for type. This process was repeated a number of times for each particular sample. The results obtained in the case where sodium palmitate was used are shown graphically[2] in Fig. 2 (XVI[3]). The curve indicates the conditions under which phase-inversion takes place. It was found that where, at low temperature, emulsions of the W/O type were formed, the soap had migrated into

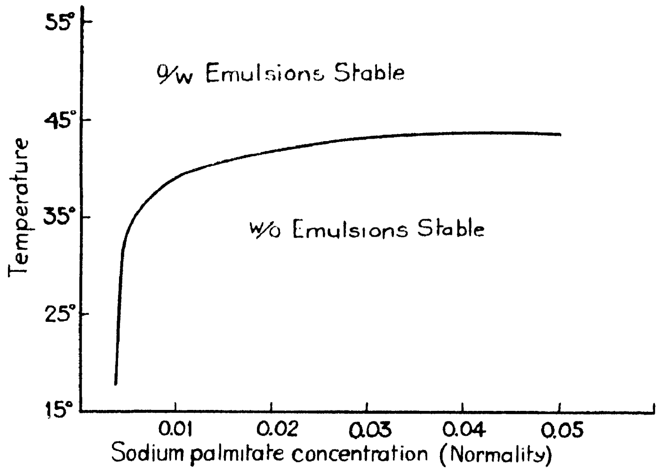

FIG. 2 (XVI[3])
Effect of temperature and of concentration of soap upon emulsion-type

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[1] *See*, for example, Aherne and Reilly, *Sc. Proc. Roy. Dubl. Soc.*, 1944, *23* (*N.S.*), 300.

[2] Wellman and Tartar, *J. Phys. Chem.*, 1930, *34*, 379.

the benzene layer (*see* Phase-partition of Soaps), forming a clear organogel system (*cf.* under 'Emulsifying Agent', Briggs' contention re type of emulsion formed when colloidal emulsifying agents are used).

The various terms used in Emulsion study can be defined as follows:

(1) **Phase-inversion.** When an emulsion of the A/B type changes to the B/A type, phase-inversion is said to have taken place. Such a phenomenon may occur, for example, when a salt of a divalent or a trivalent metal is added to an O/W emulsion previously promoted by the use of a sodium soap as emulsifying agent.

Univalent metallic ions, bivalent and tervalent anions, and alkalis, tend to sustain O/W emulsions, whereas bivalent and tervalent cations tend to sustain W/O emulsions. These two sets are, accordingly, antagonistic in their influences. W/O emulsions have sometimes been observed to undergo inversion on being warmed and shaken. Two main theories have been put forward to account for phase-inversion caused by electrolytes. One theory postulates preferential adsorption, at the interface,[1] of particular kinds of ion. If the adsorbed negative ions are in excess, O/W emulsions are sustained. If adsorbed positive ions are in excess, W/O emulsions are favoured. The other theory attributes the phenomenon to a chemical reaction, of the double-decomposition kind, which occurs at the interface. Thus, for example,

$$\underset{\substack{\text{Original emulsifying}\\ \text{agent. Sponsored}\\ \text{O/W emulsification}}}{2C_{17}H_{33}COONa} + \underset{\substack{\text{Added}\\ \text{electrolyte}}}{Mg^{\cdot\cdot}} \longrightarrow \underset{\substack{\text{Sponsors W/O}\\ \text{emulsification}}}{(C_{17}H_{33}COO)_2Mg} + 2Na^{\cdot}$$

(2) **Chromatic Emulsions.** Emulsions made from liquids of equal mean refractive indices but of widely unequal light-dispersive powers. These emulsions; accordingly, exhibit chromatic effects, the colour produced depending on the relative concentrations of the phases. If two liquids have equal refractive indices and similar optical despersive powers, transparent non-chromatic emulsions result.

If the refractive indices be not equal, emulsions of even moderate concentration, resulting from two colourless liquids (e.g. kerosene and water), will usually be milky white or pale-yellow. A method of preparation of a typical chromatic emulsion is indicated later (*see* Preparation of Emulsions).

Ramachandran [2] showed that the results of (*a*) Sethi's [3] qualitative, and (*b*) Sogani's [4] comprehensive experiments on chromatic emulsions can be accounted for by a theory which is based on the diffraction of light by a sphere immersed in a medium, where the refractive indices of the sphere and the medium are almost equal.

Scattering of Light by Dispersed Particles. *Rayleigh's Law of Light Intensities.* A law, due to Rayleigh, connecting the intensities of scattered and incident beams of light, I_s and I_i respectively, states that where the particles are small (e.g. smaller than the wave-length of ordinary light),

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[1] For accounts of experiments on the mechanism of coagulation by electrolytes of O/W emulsions, and remarks on phase-inversion *see*, for example, Martin and Hermann, *Trans. Farad. Soc.*, 1941, *37*, 30.

[2] *Proc. Indian Acad. Sc. A.*, 1943, *18*, 67.

[3] *Proc. Indian Assoc. Cult. Sci.*, 1921, *6*, 124.

[4] *Phil. Mag.*, 1926, *1*, 321.

$$\mathrm{I}_s = k\mathrm{I}_i\left\{\frac{k_1\mu_1 - k_2\mu_2}{k_2\mu_2}\right\}^2(1 + \cos^2\beta)\,\frac{n\pi\mathrm{V}^2}{a_2\lambda^4}$$

where μ_1 and μ_2 = refractive indices of the dispersed particles and the continuous medium respectively; β = angle between the scattered and incident beams; n = number of electrically non-conducting, uniform, spherical particles per ml.; V = volume of each particle; a = distance from observed particle to the point of observation; λ = wave-length of the scattered beam; k, k_1, k_2 are constants.

Tolman and others have pointed out that for larger particles (probably larger than 10^{-4} cm.), which reflect the incident light, the equation:

$$\mathrm{I}_s = \frac{k_3\mathrm{C}}{r}$$

holds when light of a given wave-length is used. Here C = concentration of the dispersed phase, r = radius of a particle, and k_3 is a coefficient which involves, amongst other factors, the value of I_i. The equation is based on the assumption that the intensity of the scattered light is proportional to the area of the reflecting surface.

(3) **Emulsifiability.** In the cases of organic liquids, the substituents in the molecule and the nature of the carbon-chain linkages exercise, in certain cases, a marked influence on the emulsifiability of the liquid. Working with aqueous soap-solutions, and with benzene and some of its derivatives, Tartar showed that the emulsifiability of such systems improved when a methyl-group or a nitro-group was present as a substituent, and disimproved when the amino-group was introduced. When the amino-group was replaced by the dimethamino-group, the inhibitory influence of the amino-group was overcome.

Emulsifiability Number (*E-Zahlen*). The number of milligrams of a fat which can be emulsified, without the use of an emulsifying agent, in 100 grams of distilled water.

(4) **Demulsibility.** The demulsibility of an oil is measured by the maximum rate at which the oil separates from a temporary emulsion, made from 1 volume of oil and 2 volumes of water under certain conditions.[1] The demulsibility is taken as a measure of the resistance of the oil to its being emulsified in the water.

(5) **Breaking of Emulsions.** Coalescence of droplets of the internal phase in such a manner that this liquid begins to separate in 'bulk-quantities'.

The Hardy-Schulze[2] valency-rule, which refers to the coagulation of suspensoids, also applies in an approximate manner to oil hydrosols. On the addition of sufficient contra-ion, the emulsion begins to clear gradually—from the bottom upwards in the case where the dispersed oil has a lower density than the water.

(6) **Creams and Creaming.** A 'cream' is a more concentrated emulsion separating, owing to the influence of gravity, from a dilute emulsion.

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[1] *See* U.S. Bur. Standards, *Tech. Papers*, 1917, No. 86, 1–37.

[2] *See under* 'Precipitation' in Section on Colloids.

Creaming becomes evident when two distinct layers, one being the more concentrated emulsion, the other being the impoverished dilute emulsion (or even the clear external phase), begin to make an appearance. Creaming should not be confused with breaking. The phenomenon of creaming is well exemplified in the creaming of fresh milk. If the internal phase has a lower density than the continuous phase, the direction of the creaming will be upwards. In the converse case the emulsion is said to ‘ cream downwards ’.

When the effect of gravity is not masked by those due to other phenomena, the globules of an internal phase obey Stokes’ Law, viz.

$$V = \frac{2r^2(d - d_1)g}{9\eta}$$

where V = limiting velocity of ascent or descent of a globule
r = radius of the globule
d = density of dispersed phase
d_1 = density of continuous phase
g = acceleration due to gravity
η = coefficient of viscosity of the continuous phase

According to this equation, creaming should not take place when $d_1 = d$. If $d_1 \neq d$ creaming may be retarded by making r as small as possible, while η is kept as large as possible. It is sometimes possible to ‘ load ’ the liquid to be used as dispersed phase by mixing with it an innocuous liquid of different density, for the purpose of making the densities of the final phases more nearly equal. The extent to which the diluting liquid should be added may be determined experimentally by finding when a drop of the mixture neither rises nor sinks when placed in the external phase. It must, however, be remembered that if the densities are equal at a certain temperature, they may not, owing to different rates of cubical expansion, be exactly equal at another temperature.

When creaming is possible it may sometimes, with advantage, be accelerated by the use of the centrifuge. Some investigators have found such a process useful. W/O emulsions with soap stabilizers usually cream rapidly.[1]

(7) **Stability of Emulsions.** This may be roughly defined as its ‘ resistance to breaking ’. Transient emulsions would have very low ‘ stability ’. Such emulsions usually result from the mere mechanical agitation of two pure immiscible liquids (i.e. without the use of an emulsifying agent). By suitable methods, however (*see later*), it is sometimes possible to prepare very dilute O/W emulsions of the stable or moderately stable variety without the use of an emulsifying agent.

King and Mukherjee,[2] who worked with O/W systems, using soaps and other hydrophilic colloids as emulsifying agents, introduced the idea of a stability factor. The stability factor of an emulsion is the reciprocal of the rate of change (with respect to time) of interfacial area, per unit area of initial emulsion-interface. In this connexion the term ‘ specific surface ’ (‘ specific interface ’, ‘ specific interfacial area ’) may be defined as the number of square decimetres of interfacial area per gram of dispersed oil.

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[1] Briggs and Schmidt, *J. Phys. Chem.*, 1915, *19*, 478.

[2] *J. Soc. Chem. Ind.*, 1939, *58*, 243 ; *ibid.*, 1940, *59*, 185.

These authors assumed that the rate of change of specific surface is proportional to the initial specific surface of the emulsion (although in the subsequent plotting of data they found, in some cases, that there appeared to be two rates—and initial rapid change, followed by a slower change), i.e. according to the simpler assumption,

$$-\frac{ds}{dt} = k_1 s_1, \text{ and } k = \frac{1}{k_1}$$

where s = specific surface ; s_1 = initial specific surface ; t = time ; k_1 = instability factor : k = stability factor. k, here, has the dimension of 'Time'.

They developed a method, based on size-frequency analyses, for the evaluation of k, and were also able to compare the efficiencies of certain emulsifying agents where the concentration of the agent was not too small. They also [1] suggested an alternative criterion of stability of certain emulsions, i.e. the 'time of half break'. This time of half break may be obtained by plotting the values of the specific surface against the time of ageing (in days), and from the graph determining the time taken for the specific surface to reach half its initial value. The greater the time of half break, the greater the 'stability' of the emulsion. The same authors commented on the apparent differences in the 'mechanism of deterioration' in similar emulsion-systems when different mechanical methods had been used in the preparation of such emulsions. King [2] reviewed some of the factors which govern the stability of O/W emulsions.

Lotzkar and Maclay [3] assumed that the rate of change (with respect of time) of specific surface, at any instant, is proportional to the specific surface at that instant, or,

$$-\frac{ds}{dt} = k_1 s, \text{ and } k = \frac{1}{k_1}.$$

k, in this case, also, has the dimension of 'Time'.

Pointing out that in many technical processes emulsions are required to withstand the effects of shaking, vibration, centrifuging, temperature-change, impact, &c., Aherne and Reilly [4] suggested that the factor, k, obtained from the formula of King and Mukherjee, or from that of Lotzkar and Maclay, might be termed a 'factor of permanence'.

Merrill [5] developed a rapid method, based on the rate of separation of the internal phase under constant centrifugal force, for the quantitative determination of the mechanical stability of emulsions. The reciprocal of the initial rate of separation, at a constant rate of centrifuging, was taken as a measure of the mechanical stability of the emulsion. The results were qualitatively in agreement with 'stabilities' measured by the rate of change of interfacial area with time method.[6] *See also* under Electro-kinetics and Emulsions.

(8) **Homogenization.** The process by which globules of the dispersed

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[1] *Loc. cit.*

[2] *Trans. Farad. Soc.*, 1941, *37*, 168.

[3] *Ind. and Eng. Chem.*, 1943, *35*, 1294.

[4] *Nature*, 1944, *154*, 86.

[5] *Ind. and Eng. Chem., Anal.*, 1943, *15*, 743.

[6] *See*, however, Aherne and Reilly, *Trans. Farad. Soc.*, 1944, *40*, 551.

phase are reduced to droplets of approximately equal diameters. The final average diameter is many times smaller than the initial average. The emulsion thus modified is said to be ‘ homogenized ’ or ‘ viscolized ’. Such homogenized emulsions are used extensively in industry, for example in the manufacture of ‘ smooth ’ ice-cream. It is found in commercial practice that homogenization usually tends to increase the viscosity of an emulsion. Sibree, however, concluded that the increase in viscosity, as a result of homogenization, is due, at least in part, to air-entrainment. It may be mentioned that the coarse emulsions formed when gum tragacanth is used as emulsifying agent are relatively viscous, while the fine emulsions resulting from the use of gum acacia are relatively mobile.

(9) **Ageing of Emulsions.** The process of allowing emulsions to stand for periods. The term ‘ ageing ’ is sometimes used, in a general way, to describe any consequent changes in the emulsions.

(10) **Wetting.** This may be defined as the tendency of a liquid to leave (after excess has been drained away) a persistent film making contact with a solid at a liquid/solid interface. A solid emulsifying agent more readily wetted by liquid A than by liquid B usually sponsors the B/A type of emulsion.

The case of solid emulsifying agents, which are probably incapable of lowering interfacial tension to a marked degree, has been treated as follows (*see* Fig. 3 (XVI³).

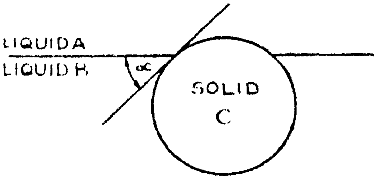

FIG. 3 (XVI³)
Case of solid emulsifying agent

Let α be the angle of contact between the solid particle C (assumed spherical) and the interface, as shown. Let σ represent the interfacial tensions. Then, for equilibrium,

$$\sigma_{CA} = \sigma_{CB} + \sigma_{AB} \cos \alpha$$

or,

$$\sigma_{AB} \cos \alpha = \sigma_{CA} - \sigma_{CB}$$

Since in all cases σ is taken to have a positive value, the sign of cos α will depend on whether σ_{CA} is greater than, or less than, σ_{CB}.

If $\sigma_{CA} > \sigma_{CB}$, cos α is positive and, accordingly, $\alpha < 90°$, i.e. most of the particle will be found in liquid B, as indicated in the diagram.

If $\sigma_{CA} < \sigma_{CB}$, cos α is negative, therefore, $\alpha > 90°$, and most of the solid particle will be found in the liquid A.

In the hypothetical case where $\sigma_{CA} = \sigma_{CB}$, $\cos \alpha = 0$, and $\alpha = 90°$. Hence half of the solid will be on the A side and half on the B side. In such a case the solid could not be effective as an emulsifying agent.

If the angle of contact were known, it should be possible to foretell the type of emulsion which would be formed, viz. A/B or B/A, using the given agent.

If the interface were studded with finely divided solid particles, it would tend to bend[1] in the direction of the liquid which wets it least, which liquid would, as a result, become the internal phase,[2] as illustrated in Fig. 4 (XVI³).

Ramsden[3] has put forward a theory dealing with the stabilities of emulsions formed when the stabilizing agents consist of solid powders (bulk-solid particles).

Bechhold and others,[4] when working with clays as emulsifying agents, considered that there is an optimum particle-size for protecting particles.

Bennister, King, and Thomas[5] found that aged aluminium hydroxide (in a form unreactive towards acids and alkalis) best approximates to an ideal solid emulsifying agent. It sponsors emulsions which, though coarse, are very stable towards added electrolytes and to temperature changes.

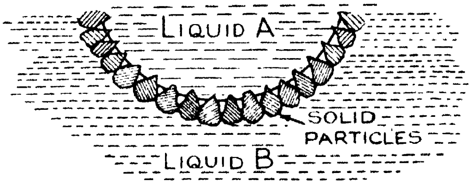

FIG. 4 (XVI³)
Finely divided solid as emulsifying agent

(11) **Surface-Active Substances.** Substances which lower surface tension. The term 'capillary-active' is sometimes employed in this connection.

(12) **Polar Substances.** Substances, such as fatty acids, containing a polar group (i.e. a group which endows the molecule with an exceptionally strong field of force, e.g. the $-COOH$ group). Polar groups are 'water-seeking', whereas non-polar groups, such as the radicle R–, are 'oil-seeking', oils being liquids of low polarity.

Harkins, Davies, and Clark believed that at an oil-water interface an added substance, such as $RCOONa$, would orient itself in such a manner that the polar group would elect to take the side of the aqueous phase, while the non-polar group would tend to take the side of the oil phase. Long polar molecules have been suggested as the best emulsifying agents for O/W systems (e.g. the proprietary substance 'Teepol').

Certain experiments, in which alcohols are used as agents, seem to indicate that, for optimum effect, a balance must be struck between the alkyl residue and the hydroxyl group.

The 'oriented Wedge' theory of emulsification, sponsored by Hildebrand and Harkins, is based on the orientation of molecules at the interface. It was held that the agent should have polar and non-polar groups. Figs. 5 (XVI³) and 6 (XVI³) illustrate the behaviour of the molecules of certain emulsifying agents, as required by this theory.

The theory implied, for example, that where the soaps, $(RCOO)_nM$, of a given higher fatty acid, RCOOH, are used as emulsifying agents, the sense and curvature of the globule should depend on (*a*) the valency *n* of the metal M, (*b*) the atomic volume of the metal. Thus, in the cases illustrated, where M = Na, $n = 1$, and the atomic volume of the unhydrated sodium ion = 23 (approximately); where M = Ca, $n = 2$, and the atomic volume of the unsolvated calcium ion = 12·5 (approximately). If, in the case of a sodium soap, the water-soluble group were to occupy more space than that which would be necessary for the closest possible packing of the hydrocarbon residues, these residues could be more closely packed if the film were to become convex on the water side. Hence the term 'oriented wedge'.

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[1] *Cf.* Richards, *J. Amer. Chem. Soc.*, 1923, *45*, 422.

[2] *See* remarks by Hildebrand, *J. Phys. Chem.*, 1941, *45*, 1303.

[3] *Nature*, 1923, *112*, 671.

[4] *Kolloid-Z.*, 1921, *28*, 6.

[5] *J. Soc. Chem. Ind.*, 1940, *59*, 226.

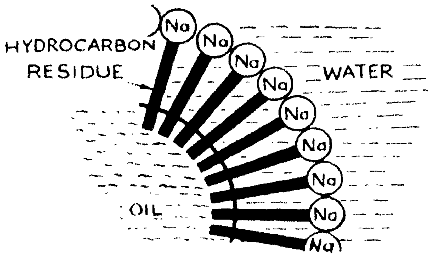

FIG. 5 (XVI³)

An O/W emulsion sponsored by a sodium soap: oriented-wedge theory

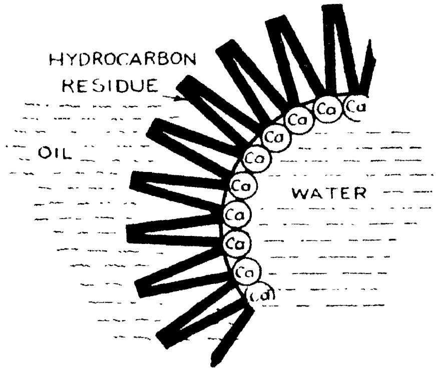

FIG. 6 (XVI³)

A W/O emulsion sponsored by a calcium soap: oriented-wedge theory

Various objections to the theory have been raised. The theory, for instance, does not explain the effects noted in connexion with Fig. 2 (XVI³). Also, since the radius of the average emulsion droplet is about 250 times as great as the length of a soap molecule, it is unlikely that the shape of the soap molecule would have such a profound influence on the curvature.

It has further been remarked that certain agents, such as finely divided carbon, contain no evident polar groups.

(13) **Peptization.** Subdivision of a gel, e.g. gum arabic, into particles much larger than molecules, or the increasing of the distances between such particles if they already exist as such, by contact with a 'peptizing agent' ('peptizer').

Bancroft suggested the use of the term peptization to describe the process which occurs when any substance is dispersed to a sol, irrespective of whether a foreign substance is or is not added to promote the process.

(14) **Interfacial Films (Interfacial Membranes).** In certain cases it has been found that an emulsifying agent forms visible (elastic) films or membranes around the globules of the dispersed phase in a stabilized emulsion.[1] One emulsification theory [2] postulated that emulsification is caused by the envelopment of the dispersed droplets by plastic films of the agent, surface tension being insignificant.

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[1] *See*, for example, Aherne and Reilly, *Sc. Proc. Roy. Dubl. Soc.*, 1944, *23* (*N.S.*), 247.

[2] Holmes and Cameron, *J. Amer. Chem. Soc.*, 1920, *42*, 2049; *ibid.*, 1922, *44*, 66.

Emulsions formed by using proteins as emulsifying agents undergo, on ageing, changes due to modifications in the mechanical properties of the interfacial film, which changes are due to denaturation of the film-material.

If certain W/O emulsions be examined microscopically, the water globules are often seen, even in the diluted emulsion, to be irregular in shape, pointing to the presence of somewhat rigid interfacial films at the interface.[1]

Cassel's theory of interfacial film stability, which is based on thermodynamical considerations, states that:

$$\mu_r - \mu_p = \frac{2\sigma}{r(\rho_d - \rho_c)}$$

where σ = interfacial tension; r = radius of curvature of the film; ρ_d = density of the emulsifying agent in the dispersed phase; ρ_c = density of the agent in the continuous phase; μ_r = potential of the curved film; μ_p = potential of the plane film.

The film can be stable only when the left-hand member of the above equation is negative and, in such an event, since σ and r are assumed positive, $\rho_d - \rho_c$ must be negative, or $\rho_c > \rho_d$.

(15) **Size-Frequency Analysis.** In an emulsion, particularly one which has not been homogenized, the globules of the internal phase may have widely varying diameters. Any statistical analysis such as the determination of (*a*) the percentage number of droplets of each different diameter, in the emulsion, (*b*) the percentage (or fraction) of the total volume of dispersed phase occupied by the globules of each different size, or (*c*) the surface-area distribution amongst globules of different size-groups, is termed a 'size-frequency analysis'. In such an analysis it is understood that all globules of diameters lying within a given arbitrary range are taken as having diameters equal to the mean value for the range in question.

(16) **Critical Ratio.** Suppose that 15 ml. of water (containing 0.2 gram caustic soda) and 85 ml. of a vegetable oil yield an O/W emulsion, while 14 ml. of water (containing the same mass of caustic soda) and 86 ml. of the oil give a W/O emulsion, then the critical ratio of water to the oil is 14·5/85·5 (i.e. 0·17 approximately), for the given mass of emulsifying agent. The numerator of the fraction is the average of 15 and 14, the denominator being the mean of 85 and 86. The exactness of such a ratio will, of course, depend on the fineness of the experimental results.

(17) **Foam or Froth.** The effect produced when bubbles remain on the surface of a liquid as a consequence of boiling, violet stirring, or aeration. A froth is a system having a relatively large gas/liquid interface, the liquid, in this case, consisting of thin films. While some foams, such as those resulting from the agitation of soap-solution, may be reasonably permanent, a foam is thermodynamically a labile system, since there is invariably present a tendency for the interface to contract to a minimum, resulting in the subsidence of the froth. Persistent foams are not developed by pure liquids. Foam-formation tendency is connected with surface-tension values, but bubble-size appears to be partly dependent on viscosity. A low rate of evaporation of the liquid is essential in the formation of persistent foams.[2]

[1] *Cf.* Schulman and Cockbain, *Trans. Farad. Soc.*, 1940, *36*, 661.

[2] *See* Ross, 'Foam and Emulsion Stabilities', *J. Phys. Chem.*, 1943, *47*, 266.

(18) **Phase-partition of Soaps.** When solutions of certain metallic soaps (e.g. sodium stearate) in water make contact with certain organic liquids (e.g. benzene), it has been observed [1] that the soap may, in part, tend to pass, through the interface, from the aqueous solution into the organic liquid, in such a way that distribution between the two phases takes place.

(19) **Solubilization.** Some substances, practically insoluble in water, may be dissolved relatively freely in solutions of detergents (e.g. soap solutions). This process is termed *solubilization.* It is not ordinary emulsification, nor is it true ' solution '. Recent investigation by X-ray technique suggests that in soap-solutions a special type of micelle develops in addition to the ionized micelles. These special micelles consist of molecular ' laminae ' of aggregated soap-molecules, the molecules within a given lamina lying substantially parallel to each other and in a direction perpendicular to the plane of the lamina, although the arrangement is not one of complete regularity. The different laminae are parallel to each other, paraffin tails of one lamina facing paraffin tails of another, and heads facing heads. When an oil such as benzene is added to the system it increases the distances between the tails, and the benzene is accommodated between these layers, with the olephilic tails of the soap-molecules dipping into the benzene. Ionized soap-molecules also play some part in the structure.

Electrokinetic Phenomena and Emulsions

It is usually held that the stability of oil hydrosols is intimately connected with ζ-potential, but much discussion has arisen as to whether or not ' critical ' values of ζ will determine stability or coagulation.

Powis, for example, in experiments performed to determine the effect of the addition of various electrolytes upon the electrophoretic mobilities of the oil-globules in very dilute emulsions of oil in water, found that coalescence of the globules occurred whenever the ζ-potential fell below 30 millivolts ($-$ or $+$). Using chlorides as the electrolytes, he found that cations of high valency were very effective in changing the ζ-potential from its original negative value (e.g. $-$ 46 millivolts) to less negative or to positive values. (*See* paper by Powis.[2])

Eilers and Korff,[3] starting from dimensional theory considerations, examined, amongst other data, the figures obtained by Powis for hydrosols (of cylinder oil) to which certain electrolytes had been added, and figures obtained by Limburg for hydrosols (of purified kerosene) to which electrolytes had also been added. In addition, some figures given by Ellis, for oil hydrosols, received attention. They concluded, from the available data on the stability of such hydrosols in the presence of electrolytes, that their own conception that the magnitude of the term $\frac{\zeta^2}{\kappa}$ determines the stability of such systems, in as far as such stability depends on boundary electric phenomena, was largely justified. $\frac{1}{\kappa}$, here, means the effective thickness of the ion-sphere. They deduced that in the case of a lyophobic colloidal system, in which the aqueous phase contains ions of valency z and concentration c, the factor which predominates the stability of the system is the energy which would be necessary to force two particles of the dispersed phase together against the action of their electric fields. For this energy they deduced the formula :

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[1] *See,* for example, Wellman and Tartar, *J. Phys. Chem.*, 1930, *34*, 379.

[2] *Z. Physik. Chem.*, 1914, *89*, 186.

[3] *Trans. Farad. Soc.*, 1940, *36*, 229.

$$c_1 \cdot \frac{\zeta^2}{10^a \sqrt{\Sigma(cz^2)}}$$

where c_1 is a coefficient and a is an evaluated index.

These authors criticized the idea of a ‘ critical potential ’.

Some indication of the proposed extension of electrokinetic theory to cases of emulsions stabilized by emulsifying agents will now be given.

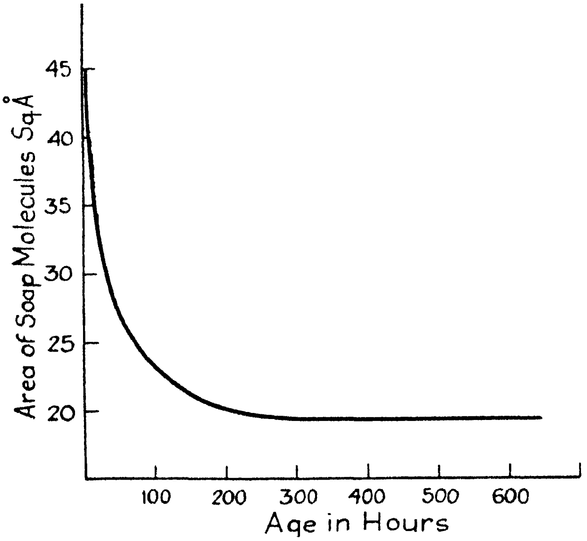

FIG. 7 (XVI³)

Variation in the molecular area of sodium oleate in emulsion

A study was made [1] of the soap-concentration in the interfacial film separating globules of paraffin-oil from aqueous sodium oleate solution (initially 0·02 N). The initial ‘ molecular area ’ of soap in the film was 44·5 Å². and this value diminished, in a regular fashion, on ageing until, after about 10 days, a steady low value of about 20 Å² was recorded. The decrease in molecular area was accompanied by an increase in the sizes of the globules. The final value of 20 Å² corresponded to a condensed monomolecular film of soap. Fig. 7 (XVI³) shows the whole effect.

Robinson [2] suggested that in such a process the ions, originally distributed in a symmetrical manner on the globule, with the paraffin residues in the oil and the hydrophilic heads towards the water, slip around the surface as the globules approach (for instance, through Brownian movement), owing to mutual repulsion, so that the parts of the globule-surfaces which immediately oppose each other contain relatively few ions. Accordingly, owing to the lowering of the ζ-potential, coalescence of the globules is favoured. When, however, the 'molecular' area is reduced in such a way that the film is condensed, or 'closest packed', ionic slip does not occur, and stability should be at a maximum. He further argued that the stability of an emulsion is not decided by the ζ-potential of the isolated globule, but by the ζ-potentials at the near faces of neighbouring globules. If this be so, it requires a higher surface-concentration of the ions to reach, or exceed, the 'critical ζ-potential' necessary for the stability of the system than it would if the stability were governed by the ζ-potential of the isolated globule alone. This happens because the 'ζ-potential-concentration' curves for the isolated globule and for the near faces of neighbouring globules follow different laws (*see* Fig. 8 (XVI[3])).

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[1] *See* Fischer and Harkins, *J. Phys. Chem.*, 1932, *36*, 98.

[2] *Trans. Farad. Soc.*, 1936, *32*, 1424.

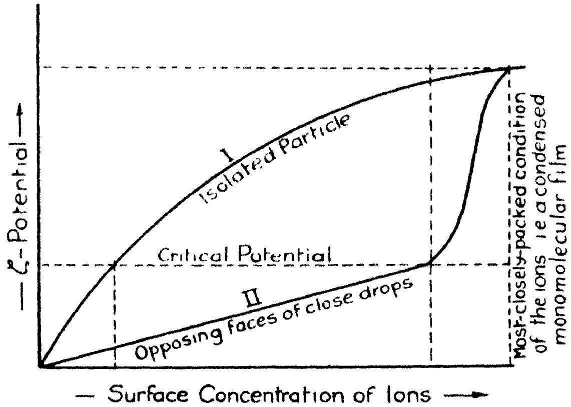

FIG. 8 (XVI[3])

ζ-potential-concentration curves

When, however, the surface-concentration increases to such an extent that its value corresponds to the most closely packed condition of the ions (i.e. a condensed 'monomolecular' film), the ζ-potential of the globule becomes equal in value to that at the opposing faces of neighbouring globules. This value greatly exceeds the critical value necessary for stability. He further held that this condition of closest-packing of ions would probably set in, in the case where emulsions are stabilized by paraffin-chain ions, when the paraffin-chain electrolyte solution causes maximum lowering of the interfacial tension.

Roberts[1] put forward a general emulsion theory in which it was postulated that the natures and concentrations of ions and of polar molecules determine emulsification, and that the interfacial region may, in fact, consist of two double layers, one in each of the phases. He considered that the emulsifying agent could no longer be regarded as a mere single substance in one phase. Accordingly, ζ-potentials are developed on both sides of the interface. He also held that there are two separate interfacial tensions, one on either side of the interface.

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[1] *J. Phys. Chem.*, 1932, *36*, 3102.

Vewrey[1] held that, since all liquids contain impurities in sufficient concentration, there is no essential difference between the natures of oil hydrosols and ordinary 'stabilized' emulsions. This author believed that electrical conditions play an important part in the stability of all categories of emulsions. Emulsifying agents are credited with shifting the potential drop of the electrical double layer towards the outer phase.

As a result of the addition of electrolytes to emulsions stabilized by saponin, sodium oleate, and other emulsifying agents, King and Wrzeszinski[2] showed that, in cases where the agent is not acted on by the added electrolyte, no evident relationship exists between the stability of the emulsion and the electric charge on the dispersed globules. The results pointed to the primary importance, from the point of view of stability, of strong interfacial adsorbed films. These authors mentioned, however, that other factors, e.g. high viscosity, may play a subsidiary part in the matter of stability.

Compare the observations of Cheesman and King[3] on emulsions stabilized by the use of certain electrolytes.

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[1] *Chem. Weekblad.*, 1939, *36*, 800.

[2] *J. Chem. Soc.*, 1940, p. 1513.

[3] *Trans. Farad. Soc.*, 1940, *36*, 241.

SECTION 2: PREPARATION

Preparation of Pure Soaps for use as Emulsifying Agents

When it is necessary to prepare pure soaps, the following methods of procedure will, for most purposes, be found satisfactory:

Sodium and potassium soaps (palmitates and stearates) may be obtained by dissolving a weighed quantity of the solid acid (AnalaR-grade) in absolute alcohol, in a round-bottomed flask. Slightly more than the calculated equivalent of AnalaR-grade caustic soda (or potash) pellets is dissolved in a further quantity of the alcohol. (*Note.*—Caustic soda is not very soluble in alcohol.) The alcoholic solution of the alkali is then added to the flask, the mixture refluxed for 1 hour, cooled (with occasional shaking), and then allowed to stand. When precipitation is complete, the precipitated soap is filtered at the pump, washed with cold alcohol, and finally washed with ether. The soap is then placed between pads in a desiccator. When dry, the soap may be preserved in well-sealed bottles.

When an ordinary solid soap is to be dissolved in water for use as an emulsifying agent, its solution in the water may be effected as follows:

The solid soap is cut into fine shavings, which are placed in a dry basin in a desiccator over calcium chloride for a period of 5 days. 1 gram of the dried material is then added to 100 ml. of air-free distilled water, at a temperature of 40°, and solution is effected at this temperature by continuous stirring. The solution, well covered, is set aside to cool, and then allowed to stand at laboratory temperature for 24 hours. The solution is then filtered through filter-paper of fairly open texture (e.g. Whatman No. 4).

In the case of oleic acid, the acid, which must generally be purified in advance by careful distillation under low pressure (B.P. 286° under 100 mm.—glass wool in the flask will prevent bumping and frothing), is added to air-free distilled water, and the calculated equivalent of aqueous caustic alkali stirred in. When the reaction is complete, the soap-solution may be made up to any requisite dilution. Precaution against undue contamination of the solution with carbon dioxide should be taken. It is always best to use freshly-made solutions.

Harkins and Zollman[1] prepared sodium oleate as follows: Oleic acid was prepared by extracting the lead salt of oleic acid (U.S.P.) with ether (lead oleate alone being soluble in this liquid), liberating the acid with hydrogen chloride, and distilling off the ether. The soap was then made by dissolving a slight excess of sodium hydroxide in absolute alcohol, filtering to remove any traces of carbonate, adding the requisite quantity of oleic acid, and refluxing for an hour. The hot solution was filtered through a heated funnel, and the soap separated from the filtrate on cooling. The solid soap was removed, washed with absolute alcohol, then washed with ether, and finally dried.

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[1] *J. Amer. Chem. Soc.*, 1926, *48*, 69.

For an account of methods used in the preparation of pure, anhydrous soaps, *see* Holmes and Maxson.[1]

Soaps of the metals magnesium, calcium, zinc, nickel, &c., may be prepared by double decomposition between the sodium (or potassium) soap in hot aqueous solution (about 90° [3]) and a hot solution of a suitable salt of the metal (e.g. zinc sulphate) containing the calculated equivalent of the metallic radicle. The mixing of the solutions should be carried out with agitation. When the reaction is complete, the mixture is cooled, and the insoluble soap removed by filtration. The precipitate, after being washed in the funnel with a little distilled water, may be further purified by grinding in a mortar [3] with separate portions of distilled water, followed by final filtration and drying. The following points are, however, noteworthy:

(*a*) Calcium, strontium, and barium soaps are hydrolysed to a slight extent on being washed with water.

(*b*) Magnesium stearate may be recrystallized from boiling alcohol.

(*c*) Nickel oleate, which is sticky when cold, may be purified by recrystallization from pyridine.[2]

(*d*) Not all these soaps are effective as emulsifying agents.

Laboratory Preparation of Emulsions

Oil Hydrosols. The following is a selection of simple laboratory methods for the preparation of oil hydrosols:

(*a*) Reflux a little of the oil with much water, for a protracted period.

(*b*) By the use of steam: A good example of the preparation of an emulsion by the use of steam is furnished in the steam-distillation of aniline.

Alternatively, about 1 gram of the oil is floated on the surface of 1 litre of air-free distilled water at room temperature, and steam is then blown, at a pressure of about 150 cm. of water, through a 1-mm. jet situated at the oil-water interface.[3]

(*c*) Use of a suitable solvent: This method is illustrated by the following experiment:

Make a 1 per cent solution of the water-insoluble oil (e.g. oleic acid) in a solvent which mixes with water (e.g. alcohol or acetone). By means of a pipette, blow about 10 ml. of this solution into 1 litre of vigorously stirred distilled water, keeping the jet end of the pipette about 10 cm. below the surface of the agitated water. By reflected light, the resultant dispersion will display a light-bluish colour. By transmitted light it will appear almost clear. Sometimes the preparation is carried out by forcing the original solution of the oil, at a temperature near the boiling-point of its solvent (e.g. alcohol), through a fine jet, into hot distilled water, followed by a period of boiling to drive off the original oil-solvent.[4] Water may then be added to any requisite dilution.

[1] *Colloid Symposium Monograph*, V, (1927).
[2] *See* Pink, *Trans. Farad. Soc.*, 1941, *37*, 181.
[3] *Cf.* Williams, *ibid.*, 1940, *36*, 1042; Dickinson, *ibid.*, 1941, *37*, 140.
[4] *Cf.*, for example, Powney and Wood, *ibid.*, 1940, *36*, 57.

Such emulsions would have a low oil-content, for example of any order up to 2 per cent. The globules therein would have diameters of orders from 0·1 μ to 4 μ. Accordingly, most of the globules will exhibit active Brownian movement.

Agent-stabilized Emulsions. For the preparation of permanent concentrated emulsions, the use of an emulsifying agent becomes necessary. The desirability of the presence or absence of a gaseous phase has been commented upon [1] by some authors. Active agitation is usually effected by some suitable means, for the purpose of assisting in the dispersal of one of the liquid phases. The following is a selection of methods followed in the laboratory :

(*a*) Shaking by hand continuous or intermittent (*see* Briggs' Process).
(*b*) Agitation by means of mechanical shakers, or by high-speed, electrically driven, 'egg-beaters'.
(*c*) Use of the mortar (*see* Pharmaceutical Method).
(*d*) Use of the Hatschek Apparatus.
(*e*) Use of a plunger, with perforated blades, which works up and down through the mixture, forcing the phases through the perforations.
(*f*) Sumner's Method.

Some of these methods will be described in greater detail (below).

It may be remarked here that it has been observed that the manner of shaking may sometimes determine the type of emulsion produced. Thus, in certain cases, gentle shaking gave W/O emulsions, while vigorous shaking gave O/W emulsions.[2] There may also be an optimum time of agitation, i.e. too much agitation (whether continuous or intermittent) may cause the emulsion to break.

Briggs' Process of 'intermittent shaking' resulted from an observation by this worker that when periods of rest were allowed between successive shakings, the total number of shakes necessary for the formation of the emulsion was very much reduced, and also considerable time was saved. The following experiment illustrates the process of intermittent shaking, the addition of the oil to be dispersed being also intermittent :

Make a solution of 0·4 gram of a good-quality gelatine in 100 ml. of distilled water, keeping the temperature at about 40°. Place 10 ml. of this solution in a 100-ml. bottle of the glass-stoppered type, and wet the walls thoroughly with the liquid. Add 2 ml. of kerosene, stopper, and shake by moving the forearm vigorously up and down the downward movement, in particular, being as violent as possible, so that the smashing-effect is audibly evident. After three of these up-and-down jerks, allow the bottle and contents to rest for half a minute. Then add another 2-ml. volume of kerosene, and repeat the process of intermittent shaking. Continue in this manner, gradually increasing the volume of kerosene added to 5-ml. quantities, until a total of 25 ml. has been added, and shaken. The final emulsion contains approximately 72 per cent, by volume, of dispersed oil. Mere rolling of the bottle and contents, with or without the addition of some glass beads, has also been found effective.

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[1] *See*, for example, Kremnev, *Kolloid-Z.*, 1934, *68*, 16 (here the presence of the gaseous phase is favoured). Contrast with this the views of Hall and Dawson, *Ind. Eng. Chem.*, 1940, *32*, 415 (working with mayonnaise emulsions, these authors found that the absence of air was advantageous).

[2] *See*, in this connexion, the effect of changing the rest-period in the intermittent-shaking method (Martin and Hermann, *Trans. Farad. Soc.*, 1941, *37*, 25). *See also* Cheesman and King, *ibid.*, 1938, *34*, 594.

Smaller quantities of emulsions may be prepared in a parallel manner using test tubes of about 30-ml. capacity. The test tubes may be sealed with corks which are covered with tin-foil.

The Hatschek Apparatus. This apparatus is illustrated in Fig. 9 (XVI^3). The pipette P carries a regulating-screw S. The long funnel F is drawn out to an approximately 1-mm. jet at its lower end. The funnel is held through a bore of a well-fitting rubber stopper, and it nearly reaches the base of the cylinder C. The aqueous medium (e.g. a 1 per cent solution of sodium oleate in water) is placed in C, filling C to about one-fifth of its capacity. The stem of F is wetted on the inside with the oil (e.g. cotton oil). A quantity of the oil is then placed in P. The apparatus is then assembled, as shown, with a loose plug of cotton-wool placed near the top to prevent the carrying over of foam. Vent V is then connected with a suction pump, and S is so adjusted that the oil drips into F at a rate equivalent to about 100 ml. per hour. By this means, oil and excess air are drawn simultaneously into the solution in C. Following this procedure, concentrated emulsions are readily made.

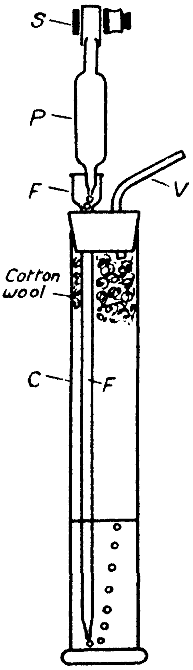

FIG. 9 (XVI^3)
The Hatschek apparatus

The 'Condensation Method' of Sumner. The apparatus used in this method is elaborate, and the applicability of the method, if the external phase is to be aqueous, is restricted to the cases of oils of boiling-points under 100°. However, by virtue of the controllability of the process, and the reproducibility of results, the method has attracted attention. In this method, for a full description of which the author's papers[1] should be consulted, the vapour of the liquid which is to be dispersed is injected, under any arbitrarily fixed conditions of temperature and pressure, through a jet of any fixed dimensions, just beneath the surface of the liquid which is to act as continuous phase, which liquid contains the emulsifying agent. Emulsions thus formed would be consistently reproducible.

Amongst the emulsifying agents popularly used for commercial purposes, triethanolamine soaps may be mentioned. Commercial triethanolamine is an almost colourless, hygroscopic, viscous liquid. Its composition, as supplied, may vary somewhat. The composition of an average sample of the commercial product would be approximately as follows:

$(C_2H_4OH)_3N$	86 per cent.
$(C_2H_4OH)_2NH$	12 per cent.
$(C_2H_4OH)NH_2$	2 per cent.

The liquid is used in conjunction with an acid, for instance oleic or stearic, for the emulsification of a wide variety of 'oily' products (including animal and vegetable oils, greases, &c.) in water. The procedure to be followed, for optimum results, will depend largely on the nature of the material to be emulsified. Handbooks, which give 'recipes' for the emulsification of typical oily substances, are sometimes available from chemical suppliers.

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[1] *J. Phys. Chem.*, 1933, *37*, 279; *J. Sci. Inst.*, 1930, *7*, 378.

Pink [1] noted that a benzene solution of triethanolamine oleate, when shaken with a small amount of water, gave a bulky precipitate of a hydrated soap, and that viscous W/O emulsions were formed when excess of water was added. If the emulsions were allowed to stand, or alternatively if sufficient water were added, the hydrated soap dissolved in the aqueous phase, and phase-inversion, took place.

Pharmaceutical Method of Making Emulsions. Carrageen Moss (Irish Moss), and the gums Acacia and Tragacanth (in powdered form), are the emulsifying agents most commonly used [2] in the preparation of pharmaceutical emulsions. Carrageen moss and tragacanth, while imparting a high viscosity to the external phase, give very coarse emulsions. Such coarse emulsions require to be homogenized before being regarded as finished products. On this account these agents are not commonly used for the making of emulsions on a small scale. Acacia is an excellent agent for the preparation of many emulsions, since it sponsors minute subdivision of the oil. It has, however, the disadvantage of being incompatible with acids, syrups, and spirituous preparations, and the addition of large or concentrated quantities of these substances will cause an acacia-stabilized emulsion to break.

There are two methods of preparation used by Pharmacists, viz. (1) the Dry Gum Method, (2) the Wet Gum Method. Following either method there are two distinct steps in the preparation :

1. The oil, gum, and water are mixed in definite proportions to form what is called a 'primary' emulsion.
2. The primary emulsion is diluted, using water, to the desired volume.

The proportions of oil, water, and gum necessary to form the primary emulsion are as follows :

For 'Fixed Oils' : 4 parts oil ; 2 parts water ; 1 part gum.
For 'Volatile Oils' : 2 parts oil ; 2 parts water ; 1 part gum.
For Oleo-Resins or Balsams : 1 part balsam ; 2 parts water ; 1 part gum.

The apparatus used consists of a clean, dry, flat-bottomed mortar, and a flat-headed pestle (a narrow-headed pestle is not satisfactory). The oil should be measured from a dry vessel, and the water from an oil-free vessel. The relative quantities already indicated should not be varied. The mixture should be triturated in one direction only, using a whipping action, not a 'grinding' one.

Dry Gum Method. Place the acacia in the mortar, and to it add the oil, with constant trituration until, after a short period, all of the oil is surrounded by particles of acacia. Prolonged trituration, at this stage, should be avoided, as the acacia would tend to become surrounded with the oil. While still triturating, add the requisite quantity of water all at once.

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[1] *J. Chem. Soc.*, 1939, p. 53.

[2] The value of Pectin, as a substitute for these emulsifying agents, is discussed by Lotzkar and Maclay, *Ind. and Eng. Chem.*, 1943, *35*, 1294.

Continue to triturate until the mixture becomes a white homogeneous paste, and the motion of the pestle against the side of the mortar gives rise to a 'crackling' sound. The primary emulsion is then formed. Continue the trituration for an additional short period and then, with constant trituration, add, first in small quantities, then in gradually increasing quantities, the water required for dilution.

Wet Gum Method. Place the acacia in the mortar. Add the water, and triturate until a mucilage is formed. Continue to triturate, and add the oil, drop by drop. If the liquid in the mortar acquires a 'ropy' appearance, and shows a tendency not to absorb the oil, add a few drops of water, and triturate again until the mixture is homogeneous. Then continue the addition of the oil, again repeating the treatment already indicated if the mixture should become 'ropy'. When all the oil has been added, triturate a little longer, and then dilute to the required volume.

The preparation of an emulsion by the Wet Gum Method requires about twice as much time as that taken by the Dry Gum Method.

Soap-Formation in situ. When soaps are used as emulsifying agents, soap-formation *in situ* is sometimes practised. For this purpose, the acid (for instance, stearic acid) is dissolved in the oil, and an equivalent proportion of the base (e.g. caustic soda) is dissolved in the water. During the process of dispersion, the soap is formed by direct neutralization. It sometimes happens that a vegetable oil (e.g. olive oil) may, of its nature, yield a soap when shaken up with a solution of a base like caustic soda.

Chromatic Emulsions. Holmes and Cameron[1] have given the following particulars of an experiment to demonstrate the formation of chromatic emulsions:

In a 4-oz. glass-stoppered bottle shake 4 volumes of an approximately 3 per cent solution of cellulose nitrate in amyl acetate with 4 volumes of pure glycerine. To the mixture, with shaking, add 2 volumes of carbon disulphide, and then more glycerine until the system becomes fairly viscous. Finally, add more carbon disulphide, with shaking, and in small quantities at the time, until colour appears when the mixture is held at some distance from the light-source. The colour may be changed progressively by the addition of increasing quantities of carbon disulphide. Creaming of the dispersed phase will occur on standing, but the colour-effects will be restored on fairly vigorous re-shaking.

Preparation of Emulsions on a Large Scale. Occasionally in laboratory practice, and usually in commercial practice, patent emulsifying machines, in which the mechanical energy is supplied by high-speed stirring, shearing-action, &c., are employed. Some colloid mills (*see* Chap XV^3, Section 2) owe their action to a shearing principle, there being two plates, one (the Stator) being stationary, the other (the Rotor) being capable of rotation at a high speed (e.g. 20,000 revolutions per minute). The clearance between these plates is small, and the mixture is forced through this clearance, thus giving a system containing fairly fine globules of fairly uniform size. Even with colloid mills, if permanence of the emulsion is to be achieved, an emulsifying agent must be used, although the amount needed may be reduced to a minimum. In some types of colloid mill both plates revolve, one in a clockwise, the other in an anticlockwise sense.

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[1] *J. Amer. Chem. Soc.*, 1922, *44*, 71.

Homogenization. For the purpose of reducing the globules of the dispersed phase to greater uniformity in size, machines termed ‘ homogenizers ’ are used. Several types are marketed, but the use of the power-driven unit is, at present, largely confined to commercial processes. In such processes, the emulsion is pumped, under high pressure, through narrow tubes against a solid surface (e.g. an agate plate), or through a valve which alternately lifts from its seating and closes again, at a high frequency. The maximum amount of opening would be a few thousandths of an inch, the valve being loaded by a powerful spring, as indicated in Fig. 10 (XVI³). Briggs [1] devised a homogenizer for laboratory use. It consists of three flasks, arranged in series, with stop-cocks between. The coarse emulsion is placed in the first flask. The second flask is evacuated to low pressure (e.g. 14 cm. of mercury). The third flask acts as a trap. The liquid enters the second flask through a tube bent at right angles, and is forcibly dashed against the inner wall of this flask. The emulsion is then returned to the first flask, and the operation is repeated until a fine emulsion is obtained.

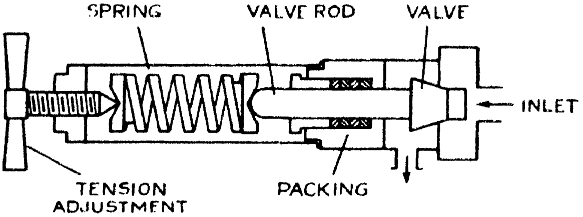

FIG. 10 (XVI³)
Principle of homogenizer

For routine laboratory purposes, ‘ cream-makers ’ will sometimes serve. A cream-maker is intended for use in the production of ‘ cream ’ from milk and unsalted butter. The coarse emulsion is pumped by means of a handle through a fine orifice, and the resultant dispersion is fairly fine. If it should be necessary to carry out the process above room temperature, the following arrangement (Fig. 11 (XVI³)) will be found satisfactory :

The apparatus illustrated consists of a metallic cream-maker, surrounded by a ‘ kettle element ’ E, contained in a metallic water-bath B. The bath carries a thermometer-post T, and a draining-tap D. The bath is supported on a stand S. V is the ‘ cream outlet ’, and R is the receiving vessel. The cream-maker is readily detachable for cleaning purposes. Leakage around the cream outlet is prevented by washers W of black-jointing and iron. P and F are the plug and flexible wire respectively. H is the pumping-handle.

Ultrasonic Waves. These have been utilized in the preparation of emulsions and a short note dealing with their nature, &c., may be given here.

Ultrasonic or supersonic waves is the acoustical term for waves of a frequency above the limit of human hearing, that is, above a frequency of about 20 kH$_z$. Modern devices are capable of generating ultrasonic waves with a frequency up to 5×10^5 kH$_z$, with a wave-length in air of $0{\cdot}6 \times 10^{-4}$ cm., of the order of magnitude of the wave-length of light.

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[1] *J. Phys. Chem.*, 1915, *19*, 210.

About the end of last century various mechanical methods of generating ultrasonic waves were devised, perhaps the most noteworthy being the Galton whistle. The effective principle of this instrument is the direction of a stream of air from a circular slit on to a circular knife-edge, and by altering the volume of air in the whistle, good standard frequencies can be obtained.

The two chief means of producing ultrasonic waves are the transformation of high-frequency electric oscillations into mechanical oscillations, by means of the Joule effect (magneto-striction) or the piezo-electric effect. The first is based on the production of high-frequency vibrations by placing a metal rod in an alternating magnetic field, when it suffers periodic changes in length, vibrating with twice the frequency of the magnetic field if previously unmagnetized. If, however, it is suitably premagnetized, the mechanical change in length will be in step with the alternating frequency.

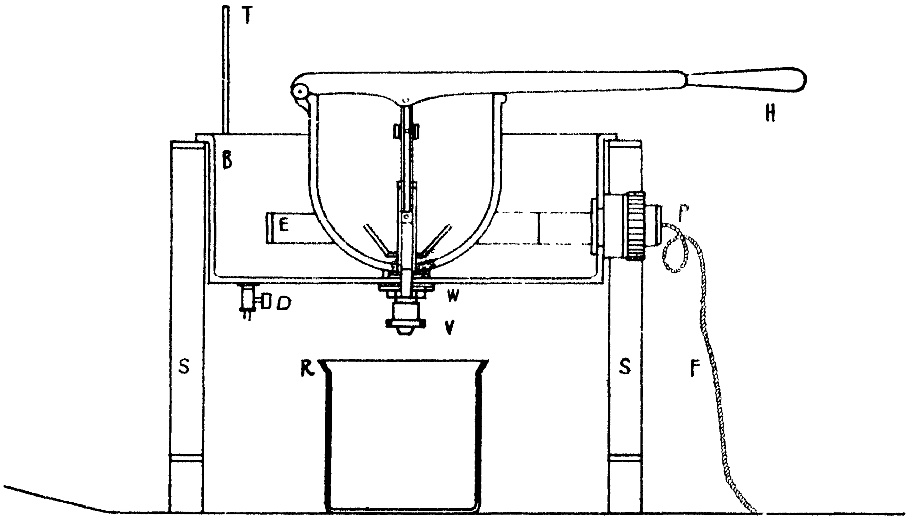

FIG. 11 (XVI^3)
A 'cream-maker'

The fundamental elastic oscillation of a rod of length l clamped in the middle gives a frequency $N = \frac{1}{2l}\sqrt{\frac{981 \times 10^5 E}{\rho}}$, where E is the modulus of elasticity in kg./mm^2 and ρ the density of the material in grams/cm^3. If now there is resonance between the natural elastic period of the rod and the frequency of the alternating current, the amplitude of the oscillation will be a maximum. An effective design for such a system is given by Pierce.[1]

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[1] *Proc. Amer. Acad. Boston*, 1928, 631 ; *Proc. Inst. Radio Eng.*, N.Y., 1929, *17*, 42.

The method which has made possible the generation of the high frequencies used in modern ultrasonic observations is due to the well-known piezo-electric effect. This phenomenon is the property of certain crystals of developing electric charges on definite crystal surfaces, when subjected to pressure or tension. If a piezo-electric quartz crystal is placed in an alternating electric field in such a position that the direction of the field is in the direction of the piezo-electric axis, the quartz will be compressed in one-half of the cycle of the field and expanded by the same amount in the other half. When there is resonance between the mechanical and electric oscillations the amplitude will be a maximum. Various adaptations of this principle have been employed in the generation of ultrasonics. Ultrasonic (supersonic) waves may be obtained when a piezo-quartz plate is made to vibrate, by electrical methods, at a high frequency (e.g. as much as 300,000 per second). The upper electrode consists of a metal ring, the lower electrode of a metal plate, the quartz plate lying in between. The whole arrangement is placed in a bath of transformer oil. The quartz plate is made to vibrate with its natural frequency by means of A.C. of corresponding frequency at from 20,000 to 50,000 volts. The energy of this vibration is communicated to the surrounding oil-bath and a vigorous movement takes place in the oil above the quartz plate. The vibrations caused by ultrasonic sound waves may influence emulsification. A vessel containing ingredients for the making of an emulsion is introduced into the above agitated oil, whereupon in certain instances dispersion readily takes place. This method of emulsification is useful in at least two respects, (*a*) excellent dispersing effect, (*b*) absence of contamination and other undesirable factors. Such qualities render the apparatus eminently suitable for scientific work. A useful laboratory supersonic apparatus is described by Porter.[1]

Wood and Loomis [2] have studied various physical and biological effects of high-frequency sound waves of great intensity. They have demonstrated the formation of permanent emulsions by such means from water and immiscible oils.

Richards [3] showed that the emulsification is of greatest intensity at the boundary surfaces between the liquid and the vibrator, and between the liquid and the walls of the vessel. Using high ultrasonic power of a frequency of 400 kHz, Rschevkin and Ostronsky [4] have produced very fine dispersions of mercury, sulphur, tin, bismuth, lead, copper, and silver, as well as emulsions of various oils and paraffins in water.

The effect of ultrasonic waves on aerosols is the opposite to that on emulsions and liquid sols. They cause coagulation of the particles. This phenomenon has been studied by Brandt and Freund [5] and Brandt and Hiedemann.[6]

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[1] *Ind. and Eng. Chem., Anal.*, 1940, *12*, 748.

[2] *Phys. Rev.* II, 1927, *29*, 373.

[3] Richards, W. T., *J. Amer. Chem. Soc.*, 1929, *51*, 1724; Richards and Loomis, *ibid.*, 1927, *49*, 3086.

[4] Rschevkin and Ostronsky, *Acta physico-chem. U.R.S.S.*, 1935, *1*, 741.

[5] Brandt and Freund, *Kolloid-Z.*, 1936, *76*, 272; *Z. Phys.* 1934, *92*, 385; 1935, *94*, 348; *Z. phys. Chem. Unterr.*, 1935, *48*, 259.

[6] Brandt and Hiedemann, *Kolloid-Z.*, 1936, *75*, 129.

Bergmann in his *Ultraschall*[1] gives an excellent account of the generation of ultrasonic waves, their detection and measurement, and deals with various applications of this technique in physical chemistry. An English translation with additions by Hatfield has been published.[2] The book contains a bibliography of 600 references.

[1] V.D.I. Verlag, Berlin, 1937.

[2] G. Bell and Sons, London, 1938.

SECTION 3: DETERMINATION OF EMULSION TYPE

Several methods have been employed for deciding whether a given emulsion is of the O/W type or of the W/O type. The following notes will indicate how some of the commoner tests are applied.

(*Note.* It is usually best to allow an emulsion to stand undisturbed for a short period (1 hour, for instance) after preparation, before applying the usual tests.)

(*a*) **The Dilution Method.** A little of the emulsion is placed on a glass plate, and a drop of water is stirred in. If the drop mixes with the sample, water is the continuous phase; if it does not mix, the oil is the continuous phase. The result is confirmed by showing that a drop of oil would mix where water would not, and conversely. The method has been criticized on the grounds that the little quantity of emulsion taken may not be a representative sample. The same test is sometimes performed by adding some of the emulsion to water, or oil, in bulk.

(*b*) **The Dye Method.** In this method a dye, soluble in one of the liquid phases and insoluble in the other, is employed to determine type.

The oil-soluble, water-insoluble dyes popularly used are Sudan III (aminoazobenzene diazotized and coupled with β-naphthol) and Scarlet R (a thioindigo derivative). A minute amount of the powdered dye is placed on the surface of a small sample of the emulsion held on a microscope slide. The sample is then observed under the miscroscope. If the colour gradually spreads, oil is the continuous phase; if the dye remains as a number of discontinuous dots, the water is continuous. Methyl violet (a rosaniline dye), Nile blue (an oxazine derivative), or potassium permanganate particles would fail to give a spreading colour with oil-continuous emulsions. The Dye Method is readily applied, but has been criticized on the grounds that an 'impurity' is being added.

(*c*) **The Electrical Conductance Method.** This method is due to Clayton,[1] and is a very sensitive one. In its simplest form, two platinum electrodes are placed at a fixed distance apart in the emulsion. A constant potential difference (e.g. 40 volts D.C.) is applied across the electrodes. Such a potential difference may be obtained from a 230-volt D.C. mains by passing the current through 6 equal lamps, arranged in series, and by taking a 'tapping' across one of the lamps. It should be noted that 6 ordinary filament-lamps, arranged as above, will not usually glow under such circumstances. The potential difference applied to the electrodes in the emulsion should operate for about two seconds. Any electrical current which passes through the emulsion may be measured by means of a milliameter which is included in the 'electrode' circuit. An O/W emulsion permits a readily measurable current to pass (e.g. about 15 milliamperes—according to the area of the electrodes, the distance between them, &c.), on account of the electrolytes which are always present (at least in traces) in the aqueous phase. On the other hand, a W/O emulsion scarcely permits any current to pass or, at most, a fraction of a milliampere.

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[1] *Brit. Assoc. Colloid Reports*, 1918, 2, 114.

A modification of this method, due to Parke,[1] enables alternating current to be used. The apparatus is indicated in Fig. 12 (XVI^3). When the medium between the electrodes is air, the note emitted from the loudspeaker is very faint. The intensity of this note is not altered when the electrodes are immersed in a W/O emulsion, but the increase in intensity is pronounced when the electrodes are immersed in an O/W emulsion. Using this method, the polarization effects resulting from the employment of direct current are eliminated. The author was easily able to follow the phenomenon of phase-inversion by the gradual change in the intensity of the note emitted.

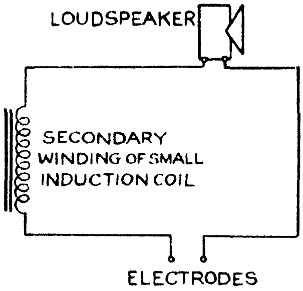

FIG. 12 (XVI^3)
Testing for type: Parke's apparatus

Other tests are also used, such as:

(*d*) **Relative Volumes of the Cream and the Impoverished Liquid.** This test is of value only when the volume-ratios of the phases are widely different, the concentration of the internal phase not being too great.

(*e*) **Direction of Creaming.** For this test there must be a difference in the densities of the two liquid phases, and the emulsion must not be so concentrated that creaming will not take place.

(*f*) **Filter-paper 'Stain'.** In the case of O/W emulsions the stain dries rather rapidly: in the case of W/O emulsions the stain will not dry.

(*g*) **External Appearance.** O/W emulsions are usually very white and opaque. W/O emulsions are sometimes yellowish, and are sometimes 'waxy' and somewhat translucent.

Additional tests have been suggested. One such test[2] is based on the differences in the indices of refraction of the component liquids. A drop, of refractive index μ_1, when suspended in a liquid of refractive index μ, will cause a parallel beam of light to converge if $\mu_1 > \mu$, and to diverge if $\mu_1 < \mu$.

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[1] *J. Chem. Soc.*, 1934, p. 1112.

[2] *Chem. Weekblad.*, 1931, 28, 251.

SECTION 4: BREAKING OF EMULSIONS

The process of de-emulsification (breaking of emulsions) is very important in certain cases, and just as there is no perfect emulsifying agent, there is no material or process which could be termed ' perfect ' for de-emulsification purposes. Numerous methods, each one effective in specific instances, are employed. They may be classified as follows :—

Methods depending on (*a*) freezing, (*b*) electrical effects, (*c*) addition, to an adequate degree, of an antagonistic emulsifying agent, or of chemicals which modify the emulsifying agent, (*d*) churning, (*e*) heating, (*f*) addition, with stirring, of excess of the internal phase, (*g*) filtration through a suitable filter, (*h*) ultra-violet light, (*i*) centrifuging, (*j*) ageing, (*k*) addition of a liquid in which both liquid phases are soluble. Some of these methods receive further attention below.

Oil hydrosols are often broken, for instance, by the adequate addition of electrolytes. The coagulation of the globules may sometimes be followed by observing the disappearance of opalescence and the appearance of a whitish turbidity.

(*a*) **Freezing.** De-emulsification by this process is sometimes very effective, the ' break ' being often perfect. Breaking in such cases appears to be caused by the effect on the emulsifying agent. In certain cases, however, the emulsions may be caused to reform on thawing out.

(*b*) **Electrical Effects.** Numerous methods, many of them patented, have been devised for de-emulsification by electrical processes. They are commonly applied in the cases of W/O emulsions. In some cases the emulsion is heated to an optimum temperature, and then subjected to the influence of a high-potential alternating electrical field. Under such conditions the water-globules rupture the enveloping oil and tend to coalesce to form larger globules. This process goes on progressively until water separates. Such methods are important in the dehydration of commercial oil-field emulsions.

(*c*) **Addition of Materials.** As an example of chemical methods of de-emulsification, the following may be cited :

' *Tret-O-Lite* ' *Treatment.* Stubborn oil-field[1] emulsions, apparently stabilized by asphaltic material, are often broken by the addition of a small volume of a dilute solution of ' Tret-O-Lite ' to the warmed emulsion, followed by stirring. Tret-O-Lite, of which the main constituent is the hydrophilic soap, sodium oleate (83 per cent), contains, in addition,

Substance	Per Cent
Sodium resinate	5·5
Sodium silicate	5·0
Phenol	4·0
Paraffin	1·5
Water	1·0

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[1] i.e. natural emulsions as produced in the oil-fields.

It was suggested [1] that the significance of the phenol might be a metathesis resulting in the formation of sodium phenoxide and the liberation of free oleic acid, which acid, dissolved in the mineral oil, was capable of attacking the emulsifying agent. The addition of a strong mineral acid (e.g. dilute hydrochloric acid) to a soap-stabilized O/W emulsion will cause the breaking of the emulsion.

(*d*) **Churning.** An excellent example of this method is the churning of cream to make butter. In this case the O/W emulsion (the cream) is broken to give a mass of fat-globules (butter) and a watery liquid (buttermilk).

(*e*) **Heating.** Heating, either direct or by steam, is practised, sometimes under pressure or after the addition of certain electrolytes, in certain de-emulsification processes. Metal at 250° is sometimes dipped into the emulsion. It has been found that the effects of heat are many, e.g. it affects interfacial tension, decreases viscosity (thus favouring coalescence), and changes the relative specific gravities of the liquid phases. Heat may also affect the emulsifying agent.

(*f*) **Addition of Excess of the Internal Phase.** If this method be attempted the agitation, for effectiveness, should be fairly violent.

(*g*) **Filtration through a Suitable Filter.** Hatschek [2] recommended the filtration method for the breaking of engine-room emulsions. One filter-bed consists of a lamina of 'amorphous' calcium carbonate, has an area of 4·5 sq. ft. and a thickness of 0·125 in. Under a pressure of 10 lb. per sq. in. it is possible to filter about 0·5 cu. ft. per minute. Adhering oil breaks away from the face of the filter, and rises to the surface. At pressures less than 50 lb. per sq. in. the apparatus continues to operate effectively.

(*h*) **Ultra-violet light** (*see* Vol. II).

(*i*) **Centrifuging.** This method is of limited value. If the densities of the liquid phases are widely different the method may occasionally be employed with advantage. It would, for instance, accelerate bulk-separation in the case of a partly broken emulsion. Previous heating of the emulsion may, by virtue of the lessening of the viscosity of the system, help the process. It is to be observed that centrifuging may merely accelerate creaming.

(*j*) **Ageing.** Soap-stabilized emulsions, after protracted ageing, may break as a result of the separation of the soap, at the interface between the phases, in the form of curds. The breaking of protein-stabilized emulsions as a result of ageing, to which reference has already been made, is a further illustration of this process of de-emulsification.

(*k*) **Addition of a Liquid in which both Liquid Phases are Soluble.** This process will appear to be similar to one of those mentioned in connexion with the preparation of oil hydrosols. The effect produced, however, under suitable circumstances, is one of de-emulsification. Violent protracted shaking of the 'continuous' type may sometimes break an emulsion.[3]

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[1] Mead and McCoy, *Colloid Symposium Monograph*, 1926, *4*, 45.

[2] *J. Soc. Chem. Ind.*, 1910, *29*, 125.

[3] *See*, for example, Aherne and Reilly, *Sc. Proc. Roy. Dubl. Soc.*, 1944, *23* (*N.S.*), 247.

SECTION 5: MEASUREMENT

The methods of measurement include the following:

(1) Measurement of Surface- and Interfacial-Tensions.
(2) Measurement of the Consistency and of the Viscosity of Emulsions.
(3) Determination of Phase-volume Concentration.
(4) Method of determining Partial Coagulation.
(5) Measurement of Demulsibility and of Emulsifiability Number.
(6) Some methods of Microscopic Observation.
(7) Examination with the Ultramicroscope.
(8) Photomicrography and Projection.
(9) A method of determining Average Diameter of Globules.
(10) Size Frequency Analyses.
(11) Molecular area of an agent at interface.
(12) Electrophoretic Mobility measurement.

Some of these methods have been dealt with in other Sections of this book.

(1) **Surface- and Interfacial-Tension** (*see* Vol. II and Vol. III (Chap. XI)).

(2) **Viscosity of Emulsion-Systems.** In general, the viscosities of emulsions vary in value, according to circumstances, from that of the pure dispersion medium to that of stiff pastes (e.g. when the concentration of the internal phase is high). In practice, various kinds of viscometer have been used in the determination of emulsion-viscosities (*see* Viscosity).

(3) **Phase-volume Concentration.** The following approximate method may be applied in suitable instances: Suppose the emulsion to be of the O/W type, and that it may be broken by the use of dilute hydrochloric acid. The procedure is then as follows:

Set up a '50-ml.' burette, and fill it from the jet to the lowest scale division (i.e. the 50-ml. mark) with dilute hydrochloric acid (3 N approximately). Add a quantity of the emulsion and note (using difference in burette readings) the volume of emulsion added. Close the mouth of the burette with the thumb, and shake the burette and contents vigorously. The emulsion will break, and the free oil will separate as a bulk layer. To assist the separation of the smaller globules, the burette may be tilted from the vertical and tapped with a pencil. The burette is clamped vertically, and the volume of the oil is read. The phase-volume concentration may then be calculated.

(4) **Method of Determining Partial Coagulation.** In a study of the partial coagulation, by electrolyte solutions, of emulsions stabilized by sodium oleate, Martin and Hermann[1] made use of centrifuge-tubes of the

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[1] *Trans. Farad. Soc.*, 1941, *37*, 30.

type illustrated in Fig. 13 (XVI³). The procedure was as follows : 7·5 ml. of the homogenized emulsion, which had been allowed to stand for 10 minutes after being made, was placed in the tube, and the desired volume of deci-normal coagulating solution (e.g. of magnesium sulphate) added. It was arranged that 1 ml. of the coagulating solution held, in each case studied, a mass of coagulating electrolyte equivalent to the sodium oleate in 7·5 ml. of the emulsion. The volumes of each given coagulating solution actually used ranged, in a series of separate experiments, from 0·2 ml. by 0·2 ml. up to 1 ml. After the addition of the desired volume, the tube was stoppered, and turned upside-down five times to ensure complete mixing. After 30 minutes, and again after 48 hours, each tube with sample was centrifuged at 2,000 r.p.m. for 5 minutes, and the volumes of the separated oil (xylene) were then read off on the graduated necks. Since the volume of oil which separated varied from one set of determinations to another, centrifuge-tubes with different internal neck-diameters were used. Determinations were usually made in duplicate. Any jelly which formed at the interface separating the free oil from the residual emulsion was included with the oil for the purposes of volume-determination. Such jellies had the greatest influence on the measured volume when a large percentage of the emulsion was broken. On re-shaking the tubes after 24 hours it was found that, in cases where 0·6 ml. (or less) of the coagulating solution had been used, the volume of the separated oil did not alter, but where more than 0·6 ml. of the coagulating solution had been used, this volume usually underwent an increase.

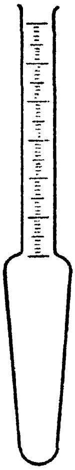

FIG. 13 (XVI³)
Determination of partial coagulation

(5) **Demulsibility and Emulsifiability Number.** The Herschel Method [1] of determining the demulsibility of a lubricating oil is briefly indicated in the following :

One part of the oil and two parts of water are stirred, at a specified speed and temperature, by means of a flat, metallic paddle, in a 100-ml. graduated cylinder, for a period of five minutes. The emulsion formed is allowed to stand at the same temperature, and readings of the volume of separated oil are taken at intervals. The maximum rate of settling, determined by the use of a Table, is termed the ‘ demulsibility ’ of the oil.

The Emulsifiability Numbers (E-Zahlen) of certain fats and oils (e.g. lard, sesame oil, beef tallow) were measured by Mészáros [2] in the following fashion : In a 100-ml. flask were placed 8 grams of the oil or fat and 80 ml. of water, the temperature being 40°. The mixture was then subjected to mechanical shaking for a period of 1 hour. The emulsion which resulted was placed in a separating funnel. The funnel with its contents were allowed to stand for a period of 24 hours, under laboratory temperature-conditions. After this period of standing, 30 ml. of the aqueous liquid were analysed for turbidity and fat-content, the results being given in terms of the number of milligrams of the fat or oil which was emulsified in 100 grams of the water without the use of an emulsifying agent. The emulsifiability number was found to vary according to the nature of the fat or oil examined. Poor emulsifiability corresponded to values below 10, very good emulsifiability to values of 50 and over.

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[1] *U.S. Bur. Standards, Tech. Papers*, 1917, No. 86, pp. 1 *et seq.*

[2] *Z. Untersuch. Lebensm.*, 1935, *69*, 318.

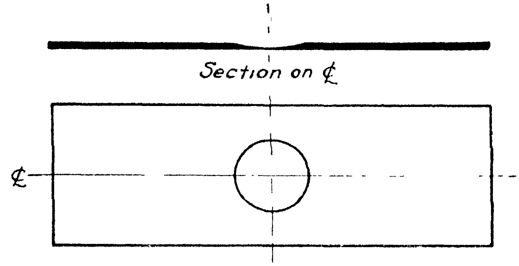

FIG. 14 (XVI³)
Slide with rounded depression

(6) **Microscopic Observation of Samples of Emulsions.** For examination under the microscope, samples of concentrated emulsions are usually diluted, by mixing gently with an adequate excess quantity of the same liquid as that which constitutes the continuous phase.[1] Flat microscope slides are sometimes employed, but slides with central rounded depressions (*see* Fig. 14 (XVI³)) are often useful in this connexion. Such slides, used with a cover-glass, permit examination in good depth, and evaporation losses are minimized. In addition, they permit the use of the cover-glass with little consequent pressure on the globules.[2] Refraction phenomena are, however, introduced.

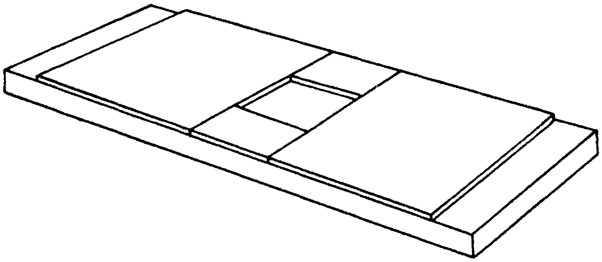

FIG. 15 (XVI³)
Slide with rectangular depression

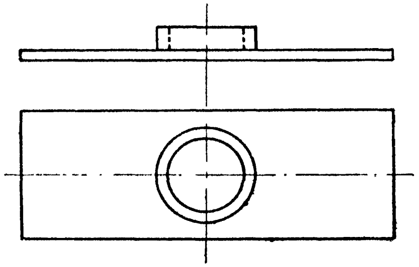

FIG. 16 (XVI³)
A 'Böttcher cell' slide

In cases where solvent-action would not interfere with the cementing-material, suitable slides may readily be made by cementing four rectangular cover-glasses, by means of Canada balsam, on to a microscope slide,[3] giving a central rectangular depression, as shown in Fig. 15 (XVI³).

Preparation of a 'Hanging Drop' Slide. A Böttcher cell (Fig. 16 (XVI³)) is commonly used in this process. The cell itself consists of a glass slide to which is fixed a glass ring so as to form a central, hollow, cylindrical container. The upper surface of the cell, upon which the cover-glass is to be placed, is first coated lightly with vaseline. A suitable cover-glass is freed from grease by being cleaned with acid and ether. To check subsequent evaporation, a few drops of the more volatile constituent of the emulsion are placed at the bottom of the cell (e.g. in the case of an O/W emulsion, a few drops of the oil could be placed in the cell). A small drop of the dispersion to be examined is placed on the dried cover-glass. The cover-glass is then inverted and placed carefully on the cell. It now carries, on its under-surface, the freely suspended drop. The drop tends to spread somewhat, so that it may be observed with a short focal-distance under a high power.

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[1] The diluent may sometimes contain a gelling agent.

[2] *See* Aherne and Reilly, *Sc. Proc. Roy. Dubl. Soc.*, 1944, *23*, 247.

[3] *See*, for example, Fairs, *Chem. and Ind.*, 1943, *62*, 374.

The Haemacytometer Slide. Haemacytometer slides have frequently been used in emulsion investigations. The essential features of such a slide, with 'Thoma' rulings, are illustrated in Figs. 17 (XVI^3) and 17A (XVI^3). Fig. 17 (XVI^3) illustrates the central portion of one model. The plane DE is slightly below the plane AB, the distance between these planes (e.g. 0·1 mm.) being etched on the slide itself. A circular hollow groove surrounds DE. The central portion C of DE is ruled with a diamond so as to give a system of small squares. The area of a single small square is also indicated on the slide. A common area for such a square would be 0·0025 sq. mm., the side of the square, accordingly, being 0·05 mm. Fig. 17A (XVI^3) illustrates the Thoma type of ruling (linear magnification of the figure = 40). Haemacytometer slides are usually insensitive to ordinary small temperature-changes. In emulsion investigations the main use of these slides has been in connexion with the determination of globule-sizes.

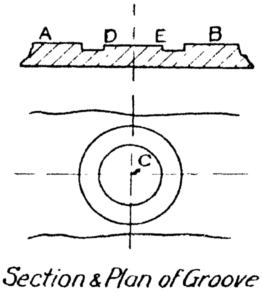


FIG. 17 (XVI^3)
A haemacytometer-slide: central portion

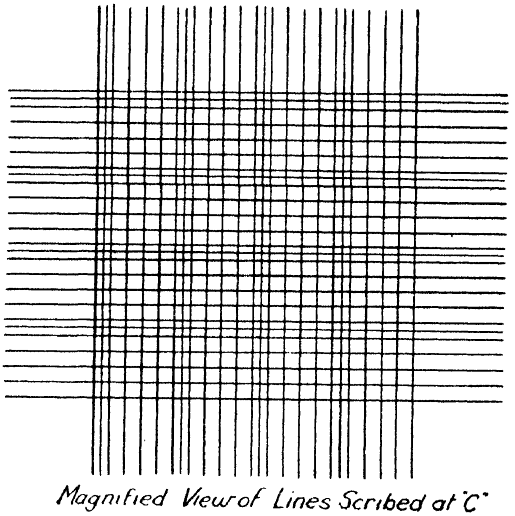
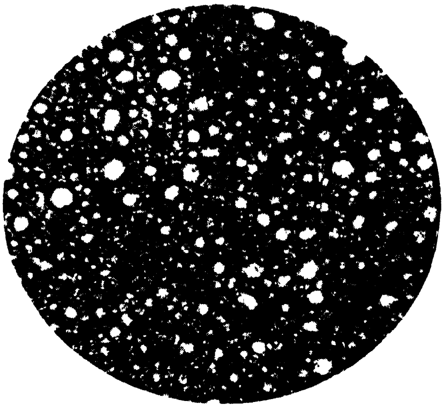


FIG. 17A (XVI^3)
Illustration of rulings (Thoma) at point 'C', Fig. 17 (Chap. XVI^3)

(7) **The Ultra-Microscope** (*see* Vol. II).

(8) **Photomicrography.** In Plate A some photomicrographs made by



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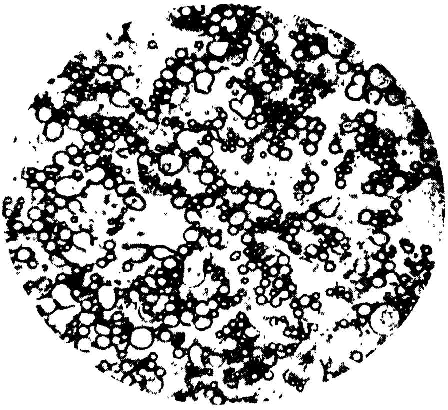

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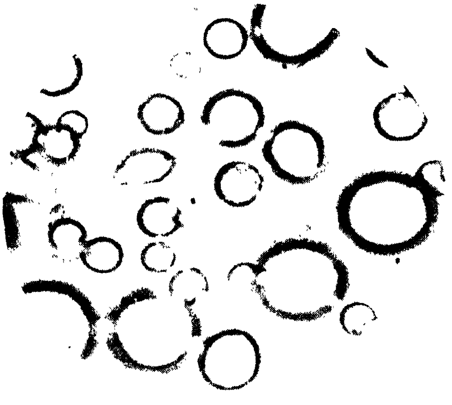

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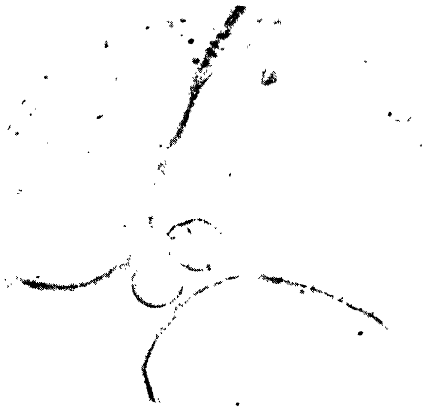

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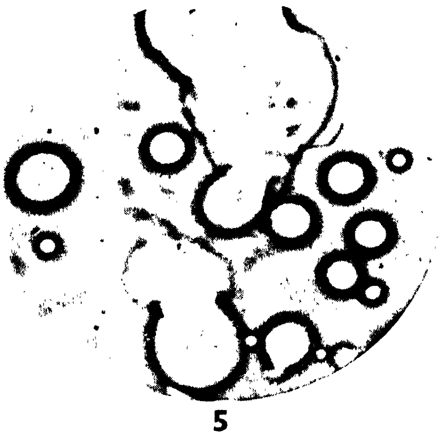

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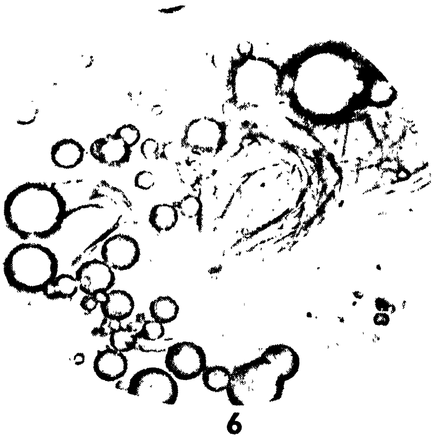

6

DESCRIPTION OF PLATE A

FIG. 1.—Water-in-liquid-paraffin emulsion—Mona wax as emulsifying agent. Without cover-glass; × 42.
FIG. 2.—Effect produced on gentle addition of cover-glass to sample; × 42.
FIG. 3.—Diluted sample of water-in-liquid-paraffin emulsion (aged 17 days). Without cover-glass; × 300.
FIG. 4.—Effect of adding cover-glass to diluted sample; × 300.
FIG. 5.—Process of interfacial-film rupture. Issuing water in focus; × 300.
FIG. 6.—Collapsed films, without water; × 300.

Aherne and Reilly in connexion with emulsion studies[1] are reproduced. The emulsion in question was of the W/O type, the oil being liquid paraffin, and the emulsifying agent being a Mona wax. Fig. 1 is a photomicrograph of a representative sample of the emulsion, × 42, no cover-glass having been used in the process of the taking of the photograph. Fig. 2 shows the effect produced on the careful addition to the same sample of a light cover-glass -- × 42. It will be observed that some deterioration occurred as a result of the addition of the cover-glass. Fig. 3 shows a representative field of a diluted sample of the emulsion, aged 17 days, no cover-glass having been used in the process of taking the photograph -- × 300. Fig. 4 illustrates the serious deterioration which resulted from the addition of a light cover-glass to the same sample -- × 300. Fig. 5 records the process of interfacial-film rupture. Water is shown issuing from a globule the film around which had just broken at one side. The same figure illustrates the coalescence of quantities of water from each of two globules, both of which had suffered interfacial-film rupture -- × 300. Fig. 6 shows some collapsed films (without water)-- × 300.

(9) **A Method of determining Average Diameter of Globules.** Various methods have been employed for the determination of the average size of dispersed particles in general, e.g.

(*a*) intensity of adsorption, and rate of solution, both of which indicate the extent of total surface of the particles ;
(*b*) measurements based on osmotic pressure, which determine the total number of particles present ;
(*c*) methods depending on dialysis ;
(*d*) methods depending on the use of X-rays, or of electro-viscous effect ;
(*e*) use of the Langmuir trough.

The following experiment[2] illustrates the application of the Langmuir trough technique to the examination of emulsion :

The apparatus used is an enamelled iron tray, similar to that shown in Vol. II, p. 529. The tray is about 5 cm. deep, and is half filled with pure water. The paper strip B may be replaced by paraffined aluminium foil. The water-surface is cleaned from contamination, and a drop (or two drops) of the concentrated emulsion is placed gently on the surface. The drop spreads with great rapidity, forming a film. The paper strip A is then used to push the film up against the aluminium barrier (to eliminate voids), and the area *s* of the film determined as in Langmuir's oil-film experiments. It is assumed that the surface layer is one particle deep, and that the globules are so small that they hold their shapes. If V = volume of emulsion used, and C = concentration (expressed as a fraction) of oil in the original emulsion, then the average diameter *d* of the globules is given by :

$$d = \frac{CV}{s}$$

'By this method, measurements of the same emulsion at two different concentrations are consistent with each other and with measurements made with varying quantities of emulsion.'

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[1] *Sc. Proc. Roy. Dubl. Soc.*, 1944, *23*, 247.
[2] *See* Contribution by Davey, *Science*, 1926, *64*, 252.

(10) **Size Frequency Analyses.**[1] Much information may be gleaned from the study of the statistics of particle size distribution in a given emulsion. Amongst the methods used in such an analysis are those involving (*a*) the employment of the microscope, e.g. the examination of the sizes and shapes of globules through photomicrographs, the use of the haemacytometer, the use of microprojection apparatus; Fig. 18 (XVI^3) shows a mode of projection with a microscope which may be used in the study of certain emulsions.[2] If so desired, the image may be projected vertically by rotating the microscope tube to the vertical position and making use of the plane mirror of the microscope to direct the light beam (*see* Vol. II, chapter on photography).

(*b*) Methods involving the 'resistance to motion' law, viz.

$$F = 6\pi\eta rv,$$

where F = frictional force between globules and the surrounding medium; η = viscosity of the medium; r = radius of the globules; v = velocity of creaming; (*c*) methods depending on the measurement of the intensity of the light scattered at right-angles to the direction of an incident beam (*see* equations given under 'Chromatic Emulsions'), or of the intensity of transmitted light.

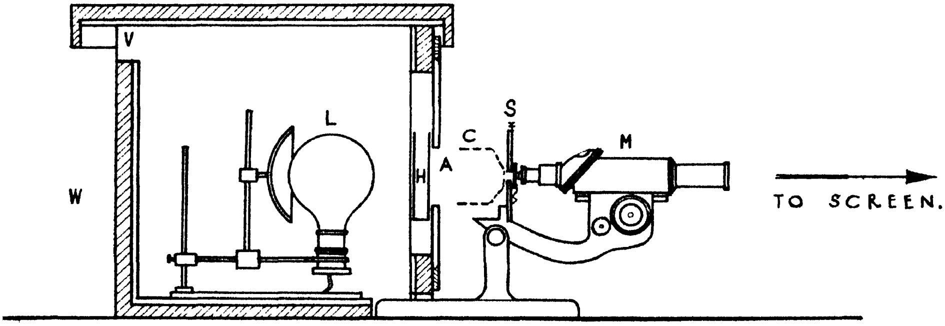

FIG. 18 (XVI^3)
Projection by means of a microscope

With regard to methods (*a*), Brownian movement and drift may usually be reduced by suitable dilution of the sample with such substances as aqueous glycerine, aqueous gelatine, gum acacia mucilage, liquid paraffin, &c.

If the principle of the ultramicroscope be used in a method of the (*a*) type, average size (only) may be determined directly, but if the ultramicroscope be used in conjunction with certain methods of the (*b*) type, it is possible to form a fair estimate of globule size-distribution.

Some methods of the (*a*) type have already been described in a previous sub-section. If, as a result of an examination of a sufficiently large number of fields, it is found that there are n_1 globules of mean diameter d_1, n_2 globules of mean diameter d_2, . . ., then the mean diameter, mean surface area, and mean volume of globules for all size-groups may readily be determined.

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[1] For a survey of the statistical methods used to describe and classify distributions, with particular reference to emulsions, *see* a paper by Cooper, *J. Soc. Chem. Ind.*, 1937, *56*, 447–53.

[2] Aherne and Reilly, *Sc. Proc. Roy. Dubl. Soc.*, 1944, *23*, 247.

Also, the relative total surface area A for all size-groups would be $\Sigma n\pi d^2$, and the relative total volume V, for all size-groups would be $\Sigma n\pi\frac{d^3}{6}$, so that the specific surface s, would be given by the expression $\frac{A}{V\rho}$, where ρ = the density of the dispersed liquid.

Curves may therefore be plotted, such as,

(α) value of n against value of d,

(β) value of $n\pi d^2$ against value of d;

(γ) value of $n\frac{\pi}{6}d^3$ against value of d;

(δ) variation of s with time.

To plot curve (δ) it would, of course, be necessary to perform several size-frequency analyses, e.g. an analysis on the freshly-made emulsion, an analysis on the emulsion after (for instance) 7 days of standing, and so on for various periods of ageing (*see* under 'Stability'). For the routine examination of batches of emulsions, Smith and Grinling[1] proposed a method involving the microscopic scrutiny, on a haemacytometer-slide carrying a cover-glass, of gelled samples which have already been suitably diluted, various squares being examined through full depth. From such a survey it is possible to calculate the number N of globules into which 1 ml. of the original oil is dispersed, from the following equation:

$$N = \frac{1000 \times n \times M \times V}{d \times a}$$

where n = average number of globules counted per square of the haemacytometer when the field is searched carefully through full depth; M = mass, in grams, of the original emulsion which contains 1 ml. of the oil; V = volume, in ml., to which 1 gram of the original emulsion is diluted; d = depth, in mm., of the ruled surface below the under-surface of the cover-glass; a = area, in sq. mm., of a single square on the haemacytometer. It is to be noted that 'large numbers of tiny globules have no more than their due effect' on the value of N. By this method it is possible to classify an emulsion as having been prepared satisfactorily or otherwise.

In applying methods (b) a certain amount of difficulty arises when the globules are so small that they exhibit Brownian movement. Blanche Koelensmid[2] discusses several methods for the determination of globule-size by sedimentation technique.

As an example of such methods, the method followed by Kraemer and Stamm[3] will now be outlined: The apparatus used is illustrated in Fig. 19 (XVI^3). The vertical tube T was slightly over 40 cm. in height. A capillary side-arm R bent as shown and terminating in a small tap-funnel, was attached at a point 29·2 cm. from the base of T, the main length of the side-arm being at a small angle θ to the horizontal. The internal cross-sectional area A of the tube T, in the region of the junction, was 4·400 sq. cm. The bend B was designed to prevent the dispersed liquid from creaming into the capillary. The apparatus was fixed to a wooden frame, as shown, and, in use, the arrangement was clamped securely to a vertical rod in a thermostat. On the frame was a spirit-level L, which was exactly horizontal when T was vertical (as judged by a plummet). Readings were taken on a glass scale (not shown) under the capillary-tube, by means of a microscope. Tube T was fitted with a stopper, through which passed a length of glass tubing drawn to a short orifice, the purpose of this arrangement being to reduce evaporation of the volatile oil (benzene). The levelling screw V, fastened to a cross-piece in the thermostat, served to adjust the level of the apparatus.

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[1] *Quart. J. Pharm. Pharmacol.*, 1930, *3*, 354.

[2] *Chem. Zentr.*, 1942, *1*, 387.

[3] *J. Amer. Chem. Soc.*, 1924, *46*, 2709.

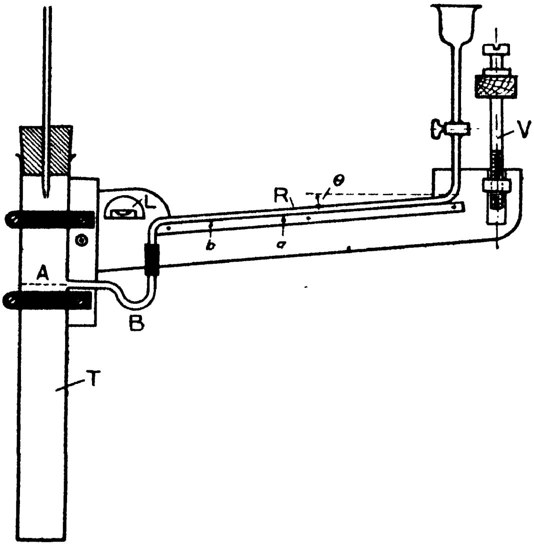

FIG. 19 (XVI[3])
Apparatus of Kraemer and Stamm

The angle θ was determined by two distinct methods. One of these methods was to clamp the apparatus so that R was horizontal, and to take measurements based on the inclination of tube T to the plummet. In the second method the apparatus was clamped in the thermostat, tube T being vertical, and water was added until the meniscus in R stood near the lower end. A glass thread, fastened to the lower end of a mounted vertical micrometer, was then lowered until it just touched the surface of the water in T. The reading on the micrometer, and the corresponding reading on the glass scale under the capillary, were recorded. The glass thread was then raised, a small additional quantity of water was added to T, and measurements were again made. By a repetition of this process it was possible, from the changes in height of the water in T and the changes in position of the meniscus in R, to determine accurately the angle θ for various lengths of the capillary. The average value of sin θ was 0·0767.

To correct for later evaporation losses, a control experiment was performed in which a layer of benzene was placed on the surface of the water in T, and the position of the meniscus in R was noted hourly for 36 hours. The meniscus was found to move down the tube steadily at approximately 0·01 cm. per hour. Emulsions of benzene in water were prepared freshly for use, under certain arbitrary conditions, using soaps as emulsifying agents. The emulsion was placed in T to a height of 39·2–39·6 cm., while the capillary side-arm contained water. The emulsion gradually creamed, the benzene globules rising past the plane A, equivalent volumes of the aqueous phase falling into the region below A. On the whole, therefore, the average density of the system above plane A decreased progressively. Accordingly, the height of the liquid in the capillary-tube progressively diminished. Making allowance for the small volume of liquid which left the capillary and entered the tube T, the rate of change of the position of the meniscus was a measure of the rate of creaming. The equation used was:

$$M = \frac{\rho_W \rho_B}{\rho_W - \rho_B}(A \sin \theta + s)(a - b),$$

where M = number of grams of benzene which had creamed, in a given time, past plane A; ρ_W and ρ_B = densities of the aqueous phase and the benzene phase respectively; s = internal cross-sectional area of the capillary; a = initial position of the meniscus in the capillary; b = position of the meniscus after the given time; A and θ had the meanings already indicated. An accumulation curve was then plotted showing the connexion between 'M' and 'time' for each emulsion studied. All the accumulation curves had the same general shape, being of the type illustrated in Fig. 20 (XVI^3). A method had previously been developed[1] for the construction of size-distribution curves from measurements made on accumulation curves. It was shown that if M = total mass of the dispersed phase which had creamed after a time t, M could be regarded as consisting of two parts. One of these parts (total mass = S) would consist of all the groups of globules of radii so large that the groups in question had already creamed completely. The other part would consist of globules of smaller

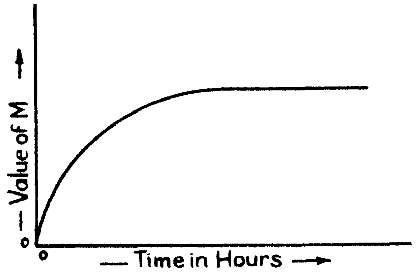

FIG. 20 (XVI^3)
Accumulation curve

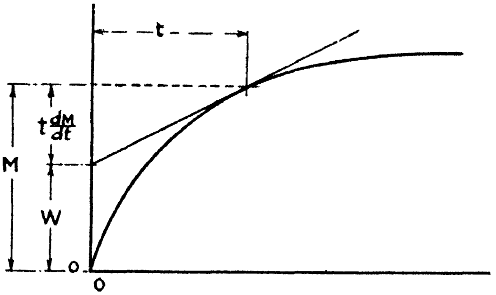

FIG. 21 (XVI^3)
Tangent to an accumulation curve

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[1] *See*, for example, 'Colloid Chemistry', *American Chemical Society Monograph*, Chemical Catalog Co., New York, 1924, p. 136.

radii which were still arriving steadily, at a rate $\frac{dM}{dt}$, in the cream-space, the groups to which they belonged having not yet creamed completely. Thus, at a given instant (after a time t),

$$M = S + \frac{tdM}{dt} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the percentage mass of particles, ds, corresponding to the radius interval, dr, of a distribution curve, the following equation was developed :[1]

$$\frac{dS}{dr} = -\frac{2t^2}{r} \cdot \frac{d^2M}{dt^2}$$

Alternatively, if a tangent to an accumulation curve be drawn at any chosen point (t, M), the value M may then be considered as the sum of two values, viz. W and $t\frac{dM}{dt}$, where $\frac{dM}{dt}$ is the slope at the point chosen (*see* Fig. 21 (XVI³)). Accordingly,

$$M = W + \frac{tdM}{dt} \quad . \quad . \quad . \quad (2)$$

On comparing equation (2) with equation (1), it is evident that

$$W = S$$

Hence by drawing tangents corresponding to suitable equal-time intervals, incremental values ΔS ($= \Delta W$) for various time-intervals (Δt) may be obtained. Values of Δr for corresponding time-intervals may be calculated from the Stokes' law equation :

$$r^2 = \frac{9h\eta}{2(\rho_B - \rho_W)gt}$$

where h = distance travelled by all globules which come from the lowest layer; η = viscosity of the aqueous medium; other symbols have the meanings already indicated. (Note—h is regarded as negative in the case of ascent.) Accordingly, $\frac{dS}{dr}$ may be plotted against r.

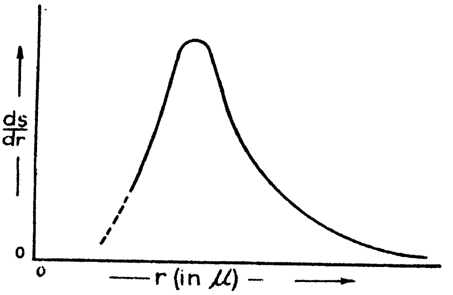

FIG. 22 (XVI³)
Distribution curve

Kraemer and Stamm gave distribution curves of the general type indicated in Fig. 22 (XVI³). The dotted portion of the curve was not obtained from actual experimental values. By measurement of the area under the curve, between the ordinates where $r = r_1$ and $r = r_2$, the actual weight of benzene dispersed as globules of radii between r_1 and r_2 could be determined. It was found, in practice, that a little of the benzene always settled out before initial observations on the apparatus could be taken. Estimates of this quantity of benzene were made. On the whole, the above method of analysis was somewhat tedious.

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[1] *Cf.* Oden, *Proc. Roy. Soc. Edinburgh,* 1916, *36,* 219.

For details of an automatic camera for recording purposes, *see* Sumner, *J. Sci. Inst.*, 1930, *7*, 398, and *J. Phys. Chem.*, 1933, *37*, 279.

To illustrate methods (*c*), the following short description of a method, due to Stamm and Svedberg[1] for the size-frequency analysis of dilute, slow-creaming emulsions, is now given:

Part of the apparatus used is indicated in side-view and in plan in Fig. 23 (XVI³). C was a glass cell, 10 × 10 × 1 cm., which, in use, contained a dilute benzene-in-water emulsion with a soap as the emulsifying agent. A black, opaque plate of bakelite was placed at the bottom of C, to minimize reflection. Another black plate was fitted into C to act as background, and this particular plate could be adjusted so that its distance from the front of C could be varied at will. C was fixed in a larger cell A, which, in turn, was cemented into a water thermostat T in such a manner that the water was in contact with all sides of the cell except the front and the top. The cell C could be photographed from the front through the slot Y. The two illumination-boxes B, B, contained 100-watt Mazda lamps. The windows, X, X, were masked to 3 × 9 cm. openings. A was painted dull black both inside and outside, and the inside of T was also blackened. T was provided with an insulated top, and the water in T was stirred by the passage through it of small bubbles of air from glass tubes.

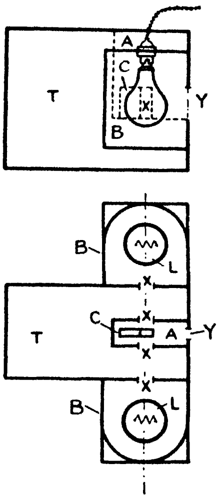

FIG. 23 (XVI³)
Part of apparatus of Stamm and Svedberg

The remainder of the apparatus (not shown) consisted of the photographic equipment and an adapted König-Martens photometer, for further details of which the original paper should be consulted. The light scattered frontwards was photographed after arbitrary periods of creaming, and the photographic densities corresponding to various cell-heights were measured, for each photograph, by means of the photometer, certain corrections being made.

The theoretical equations upon which the method was based were:

$$r = k\sqrt{\frac{x}{t_1}}$$

and

$$\frac{dS}{dr} = \frac{8\pi\rho_B}{3h}.x.\frac{dI}{dx}$$

where x = height, measured from the base of the cell; t_1 = time (in hours) which had to elapse before every benzene globule of any particular radius r had passed into the space above the height x; k = a constant; I = intensity of the light scattered to the front of the cell; h = another constant; other symbols have the same significance as in the previous case. $\frac{dS}{dr}$ was then plotted, as before, against r (in μ).

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[1] *J. Amer. Chem. Soc.*, 1925, *47*, 1582.

Construction of a First Derivative Curve from the Integral Curve. For the construction, by a simple geometrical method, of a derivative curve from the integral curve, Miss Berkman[1] proceeded as indicated in the following illustration :

Let the equation of the given integral curve (Fig. 24 (XVI^3)) be $y = f(x)$. Then $y' = \frac{dy}{dx}$ would be the equation of the first derivative curve. Also, $y = \int y'dx$. Take a point, such as P (x_1, y_1), on the integral curve. Draw the tangent to the integral curve at P. Let this tangent meet the x-axis at T, making an angle α, as shown, with the positive direction of the x-axis. Let the ordinate through P fall on the x-axis at M, M being the point $(x_1, 0)$.

In the case taken, where $x = x_1$, $y' \left(\text{i.e. } \frac{dy}{dx}\right) = \tan \alpha$. It is first required to find a point P_1 on the x_1-ordinate, such that MP_1 is merely proportional to $\tan \alpha$. For this purpose, select a suitable arbitrary ' fixed ' point, S, to the left of the origin (in practice, the point $(-2, 0)$ was chosen). From S draw a line parallel to TP. Let this line meet the y-axis at U. Then since $\tan \alpha = \frac{OU}{SO}$, $OU = SO \tan \alpha$, i.e. OU is proportional to $\tan \alpha$, and, if P_1 is the horizontal projection of U on to the x_1-ordinate, MP_1 is also proportional to $\tan \alpha$.

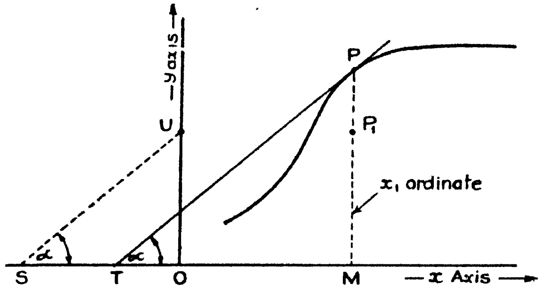

FIG. 24 (XVI^3)
First derivative curve from integral curve

To find the point corresponding to the actual value of $\tan \alpha$: Since, in practice, $SO = 2$ units, then, $\tan \alpha = \frac{1}{2}$ OU, and, accordingly, $\tan \alpha \left(= \frac{dy}{dx}\right) = \frac{1}{2} MP_1$. Hence the point now being sought is half-way between M and P_1.

This method, therefore, allows the finding of the point on derivative curve $\left(y' = \frac{dy}{dx}\right)$ corresponding to the value $x = x_1$. Similarly, by drawing tangents to the integral curve at other points and, in each case, drawing the corresponding parallel through the fixed point S, it is possible to obtain as many points on the derivative curve as may be desired. The derivative curve may, therefore, readily be constructed.

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[1] *J. Phys. Chem.*, **1935**, *39*, **527**.

(11) **Molecular Area of an Agent at Interface.** For the determination, in square Å, of the average area of emulsion-interface occupied by one molecule of adsorbed emulsifying agent (in the form sodium oleate-oleic acid—the oleic acid being due to hydrolysis) Martin and Hermann [1] used the following method :

Average globule-size was determined by diluting a standard homogenized emulsion to an adequate volume with dilute sodium oleate solution, and preparing a hanging drop slide. The microscope was fitted with an ocular micrometer (i.e. a scale, ruled on glass, which is placed between the two eyepiece lenses so that it coincides with the image formed by one of them) standardized with an objective micrometer. The objective used was a 1/12 oil-immersion type, the eyepiece being a No. 5.

From the average diameter measured, and from the phase-volume concentration of the oil, the number of globules per 100 ml. was determined and, from this, the corresponding total area of interface per 100 ml. was calculated.

For the determination of the quantity of 'sodium' and 'oleic acid' removed from the aqueous phase during the process of emulsification, a large volume of the emulsion was centrifuged, usually for 20 minutes at 1,500 r.p.m., in a carefully cleaned separating funnel. As a result, a distinct line of demarcation was obtained (in most cases) between the cream and the equilibrium liquid. The first and last portions of this equilibrium liquid were, however, always rejected. It was shown that no coagulation of globules had occurred, during the process of centrifuging, by diluting a sample of the cream obtained with some of the equilibrium liquid, and repeating the average globule-size determination.

Fifty ml. of the equilibrium liquid was then taken in a separating-funnel, and a slight excess of dilute sulphuric acid was added. The liberated oleic acid was extracted by several shakings with separate quantities of pure ether. The combined ether-extracts were thoroughly washed with distilled water until the washings were neutral to lacmoid. The ether was then evaporated, and the residue taken up with neutral alcohol. The alcoholic solution was titrated with decinormal sodium hydroxide solution, using phenol-phthalein as indicator. The aqueous layers from the extraction were also collected, and the sodium-content determined gravimetrically by the sulphate method. A check was performed using the original sodium oleate solution. From these experiments the total number of molecules adsorbed (the adsorbed material appeared in some cases to be a mixture of sodium oleate and oleic acid) per given area of interface was determined, hence the interfacial area per molecule was readily calculated.

(12) **Electrophoretic Mobility Measurement.** Methods depending on the observation, by means of the microscope (or the ultramicroscope), of the rate of movement of single globules, under a constant applied E.M.F., in a small glass cell :

One of the main difficulties in these methods lies in the fact that, since the cell is a small one, the phenomenon of electrosmosis (movement of the dispersion medium) occurs simultaneously and may, under certain circumstances, even cause the globules to travel in the wrong direction.

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[1] *Trans. Farad. Soc.*, **1941**, *37*, 25.

If the cell be so constructed that it may be regarded as a closed system, then there is no net motion of the dispersion medium in the direction of the electrodes, i.e. any of the medium which flows in one direction, close to the glass, must return along the middle portions of the cell.

The true velocity of dispersed particles may be determined by a method due to Ellis [1] who investigated the electrophoresis of dispersed oil globules (obtained, for example, by shaking pure acid-free hydrocarbon oil with pure water). In his treatment, it was assumed that in the case of a flat, closed cell, with a constant applied E.M.F., the observed velocity, $V_{obs.}$, of a globule, measured at a particular level and with respect to a fixed point on the cell wall, is equal to the algebraic sum of the true velocity, v_t, of the globule, and the velocity, v_l, of the dispersion medium (due to concomitant electrosmosis) at the same level. At any particular level, therefore,

$$v_t = v_{obs.} - v_l \quad . \quad . \quad . \quad . \quad (3)$$

Integration, over the complete cell-depth, x, gives:

$$\int_0^x v_t dx = \int_0^x v_{obs.} dx - \int_0^x v_l dx$$

For a closed cell, however, $\int_0^x v_l dx = 0$, and, since v_t is a function of the potential gradient only, and therefore constant in such a case,

$$\int_0^x v_t dx = v_t x$$

$$\therefore \quad v_t x = \int_0^x v_{obs.} dx$$

hence

$$v_t = \frac{1}{x}\int_0^x v_{obs.} dx$$

The value of v_t may therefore be determined by finding the various values, $v_{obs.}$, at different depths in the cell, and plotting the values of $v_{obs.}$ against the corresponding depths. Such a procedure results in curves of the type shown in Fig. 25 (XVI[3]), cases (*a*) and (*b*). Abramson [2] used protein-coated quartz particles in protein solutions and compared electrosmotic and electrophoretic mobilities. He found that the $v_{obs.}$-depth curve commenced at the origin. From the actual curve obtained in any one case, the value of v_t is calculated from the value of area divided by x.

In case (*a*) the 'area' means the area enclosed by the upper portion of the curve and the depth-axis, minus the area enclosed by the lower portions of the curve, the depth-axis, and the ordinates at depth = 0 and depth = x.

In case (*b*) the 'area' means the area enclosed by the curve, the depth-axis, and the ordinates at depth $= 0$ and depth $= x$. Smoluchowski[1] and Komagata[2] developed theories enabling v_t to be measured more readily. For the electrosmotic flow, in the closed flat-cell system, of the dispersion medium, the former author gave:

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[1] *Z. für physik. Chem.*, 1912, *78*, 3, 321.

[2] *J. Gen. Physiol.*, 1929, *12*, 469; *ibid.*, 1930, *13*, 657.

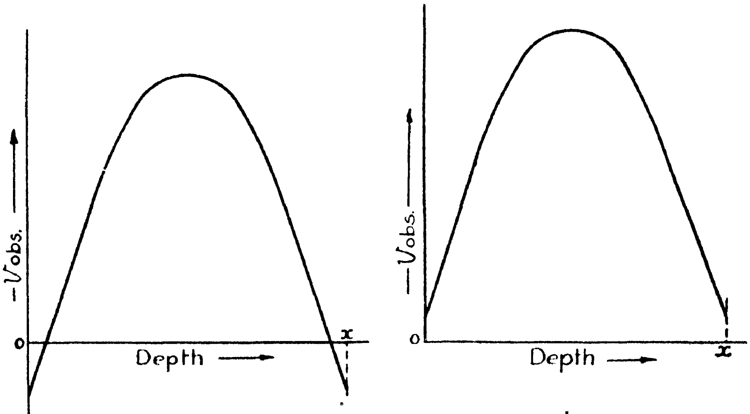
$$v_l = v_l' \left\{1 - 6\left(\frac{l}{x} - \frac{l^2}{x^2}\right)\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where v_l = velocity of the dispersion medium at the depth l
v_l' = velocity of the dispersion medium at the cell-wall
x = total cell-depth.

From equation (4), $v_l = 0$ when $\left\{1 - 6\left(\frac{l}{x} - \frac{l^2}{x^2}\right)\right\} = 0$, i.e. when $\frac{l}{x} = \frac{1}{2} \pm \sqrt{\frac{1}{12}}$, or when $\frac{l}{x} = \frac{4}{5}$ or $\frac{1}{5}$ approximately.

But, from equation (3), $v_t = v_{obs.} - v_l$, hence when $v_l = 0$, $v_t = v_{obs.}$

Accordingly, at either of the depths $\frac{4}{5}x$ or $\frac{1}{5}x$ (approximately) the observed velocity corresponds to the true velocity. These depths are often called 'stationary levels', since at these particular levels there is no electrosmotic movement of the dispersion medium.



(a) (b)

FIG. 25 (XVI³)
Variation of observed velocity with depth

As an alternative to the observing of the globule-velocity at either of these depths, the velocities at two other depths, for example $\frac{1}{6}x$ and $\frac{1}{2}x$, could be determined, and v_t then evaluated by treating equations (3) and (4) as simultaneous equations.

Komagata showed that where the width of the flat cell is comparatively great the above theory is valid. Where, however, this is not the case, i.e. where the depth of the cell is relatively considerable, the stationary levels are given by the equation :

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[1] *See* Graetz, *Handbuch der Elektrizitat und der Magnetismus*, Leipzig, Barth, 1921, Vol. II, p. 366.

[2] *Researches Electrotech. Lab.*, Tokyo, 1933, p. 348.

$$y = \pm \frac{x}{2}\sqrt{\frac{1}{3}\left(1 + \frac{384}{\pi^5 k}\right)}$$

where y = the level measured from the central axis ; x = the complete depth ; k is the ratio of one-half the width to one-half the depth.

Method of Focusing at a Given Depth in a Cell of Rectangular Cross-section. The usual practice is to obtain the microscope fine-adjustment readings corresponding to the top and bottom internal surfaces (when these surfaces are correctly in focus), and to find, by linear interpolation between these readings, the fine-adjustment reading corresponding to the level at which it is desired to focus.

Electrophoretic mobility (u) is usually expressed as the velocity of the globule (or other particle) in microns per second under a potential gradient of 1 volt per cm., i.e. the velocity of migration (in microns per second) divided by the potential gradient (in volts per cm.). Thus expressed, it is found that the electrophoretic mobility is independent of the applied field.

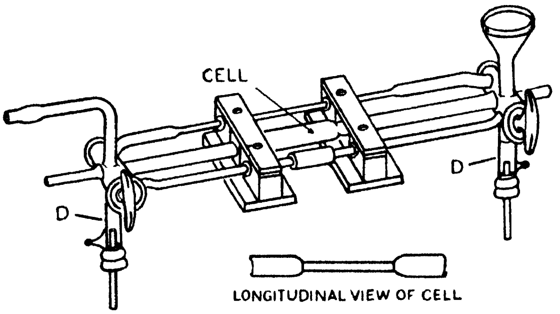

FIG. 26 (XVI³)
Abramson's flat cell for electrophoresis measurement

Apparatus used in the 'Microscopic' Method. Ellis used a flat layer of liquid between two glass plates provided with electrodes near their ends. He then determined the true electrophoretic velocity by the 'integration method', as already described. Fig. 26 (XVI³) is an illustration of the type of flat cell devised by Abramson[1] for microscopic' electrophoresis measurement. It is a modification of an arrangement due to Northrop and Kunitz.[2] In one model the cell was 3·5 cm. long, 0·99 cm. wide, and it had an average depth of 0·081 cm. The cell is made of one piece of glass, and is readily cleaned with caustic soda solution, dilute acid, or other cleaning liquid. Reversible electrodes, viz. copper in copper sulphate solution, are inserted in the electrode-vessels which are fused to the cell. The side-arms are so constructed that agar or plaster of Paris plugs may be introduced into the electrode-vessels at points D. Such plugs prevent the complications which would otherwise be caused by the streaming or diffusion of the copper sulphate from the electrode-compartments into the side-arms. The apparatus rests directly on the slide-stage of the microscope, and may be inverted when necessary.

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[1] *J. Gen. Physiol.*, 1928, *12*, 469 ; *ibid.*, 1930, *13*, 657 ; Abramson and Grossman, *ibid.*, 1931, *14*, 563.

[2] *Ibid.*, 1925, *7*, 729.

Fig. 27 (XVI³) illustrates a further modification [1] of the apparatus, in which the cell is held vertically. A Pyrex all-glass microelectrophoresis cell is described by Briggs,[2] who also describes (*loc. cit.*) electrical circuits, including a vacuum-tube voltmeter (for measuring field-strength), which may be used in conjunction with the cell when organic liquids of low specific conductivity are placed in the cell. The use of stop-cock lubricant is not essential in this particular apparatus.

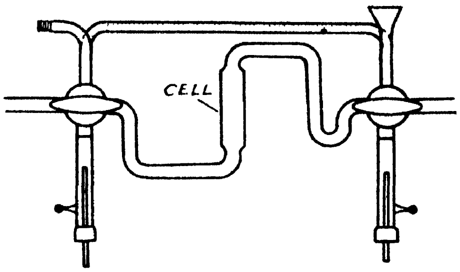

FIG. 27 (XVI³)
Vertical cell for microscopic electrophoresis

Some cells used in recent important determinations of the electrophoretic mobilities of globules in emulsions will now be described :

Powney and Wood,[3] in experiments on the electrophoretic mobilities of the oil drops in detergent solutions, used an apparatus of the type devised by Smith and Lisse.[4]

The Smith and Lisse apparatus is illustrated in Fig. 28 (XVI³). It is a closed system containing two glass capillary-tubes T_1 and T_2, of which T_1 has the narrower bore. These capillary-tubes are fitted, at either side, to cylindrical glass tubes, about 2 cm. in diameter, each containing a platinum electrode. The tubes T_1 and T_2 are carefully selected so that T_2 acts as return tube for the electrosmotic flow of the dispersion medium, i.e. the electrosmotic return-flow which would normally take place in the central regions of a single-tube cell would, in this apparatus, take place in the tube

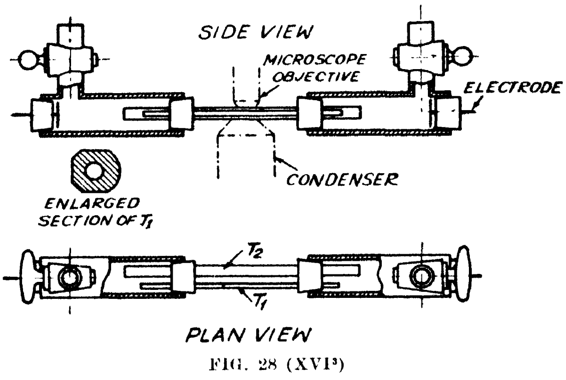

FIG. 28 (XVI³)
Smith and Lisse cell

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[1] *See* Abramson, Moyer, and Voet, *J. Amer. Chem. Soc.*, 1936, *58*, 2362.
[2] *Ind. and Eng. Chem., Anal.*, 1940, *12*, 703.
[3] *Trans. Farad. Soc.*, 1940, *36*, 57.
[4] *J. Phys. Chem.*, 1936, *40*, 399.

T_2. There is, therefore, no movement of the dispersion medium along the axis of the tube T_1, so that the 'observed' velocity of globules along this axis (depth $= 0{\cdot}5d$, where d is the internal diameter) is equal to the velocity of the globule relative to the dispersion medium. In other words, this observed velocity is equal to the 'true velocity', since the axis of T_1 is a stationary level.

(*Note.*—In the case of 'single-tube' cells of cylindrical cross-section, the stationary levels would, according to Smoluchowski, be at depths $0{\cdot}146d$ and $0{\cdot}854d$, i.e. the true electrophoretic velocity of globules (or other particles) can be directly observed at points in that annular region which is at a distance of $0{\cdot}707r_1$ from the axis of the cylindrical tube, where r_1 is the radius of the tube.)

Powney and Wood determined the true velocity by taking the times of passage of a number of different globules (of Nujol) between two calibration lines on the eyepiece of the microscope, due precaution being taken to avoid focusing-error (*see* note on Focusing (p. 446)). A thermometer was incorporated in the apparatus for direct temperature-reading. The applied voltage could be varied from 0 to 250 volts (D.C.), the actual voltage used depending on the order of the measurement. It was initially shown that the electrophoretic mobility was independent of the applied voltage. A high-resistance Ferranti moving-coil voltmeter was employed for voltage-measurement. The greatest current used in the series of experiments (i.e. in the case of the system of maximum conductivity) did not exceed 0·5 milliampere, and in the vast majority of the experiments the current used was considerably less than this. Heating effects were therefore negligible. Occasionally, during the investigations, readings were interrupted and the capillaries flushed by suction applied to one side of the cell. In this manner several samples of the given emulsion were examined. In preliminary experiments it was found that the electrophoretic mobility of Nujol in pure water (conductivity $= 2 \times 10^{-6}$ ohm^{-1} cm.) was 4·35 μ/sec. per volt/cm. towards the anode, the temperature being 25°. The actual experiments were performed at room temperature, and then calculated for 25° C. on the assumption that the mobility varies inversely as the viscosity of the dispersion medium. In both preliminary and subsequent experiments (e.g. when the dispersion medium consisted of very dilute solutions of sodium chloride, sodium hydroxide, sodium dodecyl sulphate, &c.) the viscosity of the dispersion medium was taken to be substantially the same as that of water at the same temperature. The same authors used a similar apparatus in another set of experiments.[1]

King and Wrzeszinski,[2] in investigations on factors in the stabilization of emulsions, carried out measurements of the electrophoretic mobilities of the globules in homogenized, agent-stabilized emulsions, using an apparatus substantially similar to that used by Bennister and King [3] which, in turn, was modelled on the technique of Mattson and Mooney,[4] involving the ultramicroscope principle.

The apparatus of Bennister and King is indicated in Fig. 29 (XVI[3]).

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[1] *Cf. Trans. Farad. Soc.*, 1941, *37*, 152 and 220.

[2] *J. Chem. Soc.*, 1940, p. 1518. [3] *Ibid.*, 1938, p. 991.

[4] *J. Phys. Chem.*, 1928, *32*, 1532; *ibid.*, 1933, *37*, 223; *Phys. Rev.*, 1924, *23*, 396.

The horizontal cell, of thick-walled Pyrex glass tubing, was 22 cm. long and had an internal diameter of 2·0 to 2·5 mm. At D the horizontal tube had its upper surface ground flat to within 0·25 mm. of the inner wall and, at right angles to this flat surface, another plane surface was ground (*see* sectional view). Both of these surfaces were well polished. Attached at the ends were the wider vessels (B, C) carrying sealed-in platinum electrodes (E, E) held as close as possible to the bore of the horizontal tube. F and F′ were well-fitting stop-cocks, F being used for filling purposes and F′ for emptying. The cell could be cleaned and steamed-out (to remove any traces of electrolytes which might be adsorbed on the glass) before each experiment.

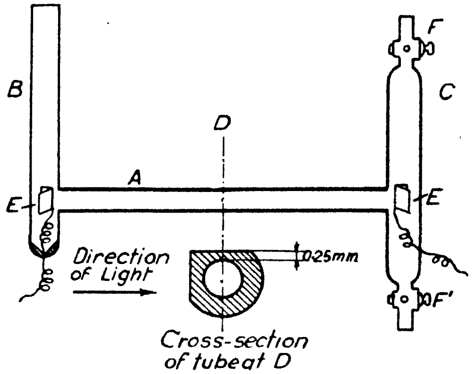

FIG. 29 (XVI[3])
Bennister and King cell

In use, the cell was clipped to a wooden block, and the block, in turn, was rigidly fixed to the microscope-stage. The dispersed particles in the electrophoresis-tube were illuminated by the light from a high-power electric lamp, the light having previously been passed through an alum solution for heat-absorption (King and Wrzeszinski illuminated the oil-globules in the tube by means of an intense 6-volt microscope-lamp and, for the 'spare' microscope-objective, used an objective of medium power). The light was brought to a focus at D, just directly below the microscope which was used for observation. The 'spare' microscope-objective was fixed to a movable metal arm, attached to a Vernier scale, and it could be moved up and down by means of a screw. It was thus possible to observe at any desired depth within the electrophoresis-tube. The eyepiece of the microscope was fitted with parallel wires at a known distance apart, and the potential gradient in the tube was checked occasionally by the use of an electrostatic voltmeter.

In the experiments on emulsions, the authors used a 110-volt D.C. supply, and they noted, by means of a stop-watch, the time taken by individual globules to cover the distance between the parallel wires. By reversing the polarity, the experiments were repeated with the globules moving in the opposite direction. The mean of the velocities from twenty observations—ten in each direction—was considered satisfactory in any one experiment. The stationary level[1] (zero electrosmotic flow) was determined as exactly as possible by experimental methods. The authors encountered little Brownian movement during the series of experiments on emulsions, whereas Bennister and King, working with charcoal particles, sometimes failed to follow a given image through the complete distance owing to the phenomenon in question.

The theory of a two-path rectangular microelectrophoresis cell (the equivalent of the Smith and Lisse cell (already described) but rectangular in cross-section) is given, and a simple method of constructing such a cell is indicated, by Beniams and Gustavson.[1]

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[1] *See* previous note on stationary levels in 'single-tube' cells.

Focusing-errors. Two general methods have been employed for the experimental location of a desired level of observation within a cell, viz. (*a*) by adjusting the relative positions of the cell and the illuminating beam (when the cell is illuminated horizontally) so that only the desired level is illuminated, (*b*) by adjusting the position of the 'viewing' microscope-objective so that only the desired level is in focus.

(*Note.*—The procedure followed when applying method (*b*) to the case of a flat rectangular cell has already been outlined.)

Electrophoresis tubes, of both the 'single-tube' and 'double-tube' kinds, with cylindrical bores and flat external faces, have just been described. In the case of 'single-tubes' of cylindrical bore, the stationary level, as already pointed out, is an annular zone distant $0{\cdot}707r_1$ from the axis of the bore, i.e. $0{\cdot}293r_1$ below the highest (or above the lowest) point of the bore, assuming that the tube is placed horizontally.

When either of the above level-locating methods, or both conjointly, are applied to such cells, certain difficulties may arise, since the 'working' glass walls of the cell constitute plano-convex cylindrical lenses separating air from the dispersion-system under investigation. One of these lenses will, in general, refract the illuminating beam, and the other will refract the viewing beam.

With regard to the location of a level in such cells by method (*a*) above, Boswell and Larson[2] showed that if the illuminating-beam enters the 'single' type of cell from one side, at a position corresponding to the upper stationary level, it will be bent upwards to a position $0{\cdot}195r_1$ below the highest point of the bore. If the microscope is focused on this position, in the belief that the stationary level is actually in focus, the resulting measurements will be unreliable. These authors showed that, to illuminate at the upper stationary level zone, the beam must enter from the side at a distance $0{\cdot}377r_1$ below the highest point of the bore, and not at a distance $0{\cdot}293r_1$ below this point. Further, the illuminated region within the dispersion system is not horizontal, but is tilted.

Henry[3] pointed out a more deceptive error, which could result from the employment of method (*b*) for the location of a desired level in a cell with a flat upper surface and a cylindrical bore, i.e. when it is attempted to locate the desired level by the use of the fine focusing-adjustment of the microscope. This author gave the following equation, connecting the 'actual' point of focus of the objective and the point of focus of the same objective in air:

$$\frac{\mu_1}{p - \mu_1 k/\mu_2} = \frac{\mu_3}{q - k} + (\mu_2 - \mu_3)$$

where μ_1, μ_2, μ_3, are the refractive indices of air, the glass of the cell, and the liquid-system in the cell, respectively, and, if r_1 be the radius of the cylindrical bore, kr_1 is the thickness of the glass between the top plane surface of the cell and the highest point of the cylindrical bore (assuming, as before, that the cell lies horizontally) pr_1 and qr_1 are the distances, respectively, below the same top plane surface of the positions of the focal points ' in air ' and in fact.

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[1] *J. Phys. Chem.*, **1942**, ***46***, **1015**.

[2] *Ibid.*, **1936**, ***40***, **833**.

[3] *J. Col. Sci.*, **1938**, **997**.

To illustrate the use of the equation : Assume that a cell of the ' single-tube ' type, with a cylindrical bore, and a flat upper surface, is being used. Suppose that the reading of the microscope fine-adjustment is taken when the top plane surface of the cell is in focus. Assume that it is required to focus the objective on the stationary level within the cell. In this case, qr_1 will be the distance of the stationary level below the top flat surface, and $(q - k)r_1$ will be the distance of the level in question below the highest point of the bore.

Hence $(q - k)r_1 =$ either $0{\cdot}293r_1$ (upper stationary level),
or $1{\cdot}707r_1$ (lower stationary level),
whence $(q - k) =$ either $0{\cdot}293$ or $1{\cdot}707$, depending on which of the two stationary levels it is desired to focus.

By substituting in Henry's focusing equation (above) the actual values of μ_1, μ_2, μ_3, k, for the given assembly, and inserting the desired value of $(q - k)$, the value of p may be calculated and, from this, the value of pr_1 may be ascertained.

This value, pr_1, gives the change which must be made in the microscope fine-adjustment reading in order that the desired level should be correctly in focus.

'Moving Boundary' Method of Observation and Measurement of Electrophoresis. The phenomenon of electrophoresis may be observed by the use of an apparatus similar to that depicted in Fig. 30 (XVI³). To illustrate the use of such an apparatus the following experiment may be performed : With the tap S_3 opened a sol (e.g. of ferric hydroxide or of gamboge) is introduced through the funnel F as far as the two taps S_1 and S_2. About 5 ml. of distilled water is poured into each of the tubes T_1 and T_2. S_3 is then closed, and S_1 and S_2 are opened. S_3 is now opened very slowly until the boundary between the distilled water and the sol lies about half-way in each of the tubes T_1 and T_2. S_3 is then closed again. A D.C. mains potential of about 230 volts is next applied by means of platinum electrodes at the top of the water columns. The boundaries will move slowly, one rising and the other falling. One of the moving boundaries will become hazy, and the other will appear to move at a rate of about 0·5 cm. in 10 minutes. After 10 minutes the polarity may be reversed, and observations made in the opposite direction.

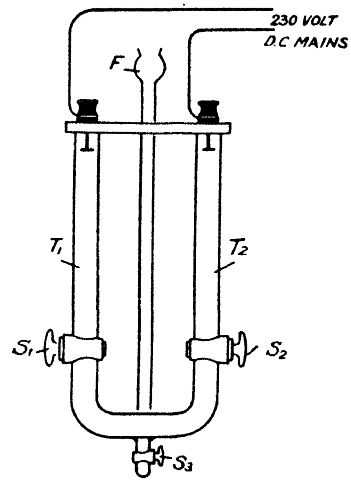

FIG. 30 (XVI³)
A simple 'moving-boundary' apparatus

For the determination of the electrophoretic mobility by the method of the moving boundary a number of refinements in the apparatus must be made, e.g. to avoid errors due to electrolysis, to enable the actual potential gradient under which the boundary is moving to be determined, and to permit the location of the boundaries when they cannot be observed directly by colour differences.

One method of avoiding errors due to electrolysis is indicated in connexion with Fig. 31 (XVI[3]). With regard to the potential gradient, it is evident that the potential could not fall uniformly along the whole length of a system such as that already described for use in the apparatus illustrated in Fig. 30 (XVI[3]), nor could a completely uniform potential gradient be readily maintained even by altering the nature of the supernatant (overlying, indicating) liquid. Mukherjee [1] essayed to overcome this difficulty by measuring the potential difference across the boundary itself by the use of reversible electrodes inserted in small side-tubes sealed to the U-tube. Kruyt [2] calculated the mobility of the assumption that the rising boundary moves in a medium of conductivity equal to that of the supernatant liquid, while a falling boundary moves in a medium of conductivity equal to that of the original sol. Hacker [3] eliminated the difficulty by first calculating approximately a correct concentration of the supernatant liquid with respect to the ions of a salt BC (where similar ions are contained in the sol system), and then determining by trial, using slightly varying concentrations, the actual concentration necessary to give a conductivity of the advancing column (as measured from the drop of potential across two Mukherjee side-tubes) equal to that of the original sol. The method, although time-consuming, gives satisfactory results.

Henry and Brittain [4] developed mathematically a theory of moving boundary electrophoresis, and showed that extreme caution should be observed in the use of 'artificial' supernatant liquids. They suggested that the ultrafiltrate is the only suitable liquid to employ with sols where the composition of the intermicellar liquid is unknown. These authors suggested that where Hacker's method is inconvenient, and the ultrafiltrate is used as the supernatant liquid, the following simple equation could be used, especially if the change in concentration of the advancing sol column be not considered significant, to calculate the mobility:

$$v_A = \frac{iu_A}{\kappa}$$

where v_A is the velocity of the advancing sol column, i is the current density, u_A is the mobility of the particles, and κ is the specific conductance of the advancing sol column measured, during its motion, by means of suitably placed Mukherjee side-tubes. In actual experiments (*loc. cit.*) the authors had used a moving boundary apparatus of the type recommended by Kruyt.

For the location of boundaries when they cannot be directly observed by colour differences, the movement of the boundary may be followed by means of a Tyndall beam, or the phenomena of absorption of ultra-violet light and of fluorescence caused by ultra-violet light may sometimes be employed to advantage.

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[1] *Proc. Roy. Soc. A.*, 1923, *103*, 102. *See also J. Phys. Chem.*, 1932, *36*, 595.

[2] *Kolloid-Z.*, 1928, *44*, 22.

[3] *Ibid.*, 1933, *62*, 37 and 66.

[4] *Trans. Farad. Soc.*, 1933, *29*, 798.

One form of moving boundary apparatus which has been used in recent investigations[1] on emulsions is that described by Price and Lewis.[2] This apparatus is represented in Fig. 31 (XVI³). The tube is made of quartz. To prevent polarization-products from migrating into the main U-tube, this tube is fitted with two side-arms, X and Y. The glass funnel with tap is attached to the filling arm by a ground glass-quartz joint. To prevent gassing at the main electrodes in the side-arms, the anode consists of a solid cylinder of zinc, and the cathode consists of a hollow cylinder of lead on which lead dioxide is 'formed' as follows: The electrodes are placed in 20 per cent sulphuric acid and submitted to intermittent reversal of the current (20 ma.) for 3 days (after fully charging at 20 ma., the authors found that at a discharging rate of 10 ma. the capacity of an electrode was 8 ma. hours—this capacity was ample for the purposes of their experiments). The length of the side-arms is sufficient to prevent any ions liberated at the electrodes from migrating into the main tube (thus, in practice, the authors used a potential gradient of about 2 volts per cm., operating for 30 minutes, the effective length of each side-arm being about 15 cm.). Accordingly, any change in ionic concentration with consequential change in resistance is restricted to the side-arms. The electrodes LM in the main U-tube are small platinum wires (platinum disks are to be avoided) adjusted to marks on the tube, the effective distance between the marks being determined by conductivity measurements.

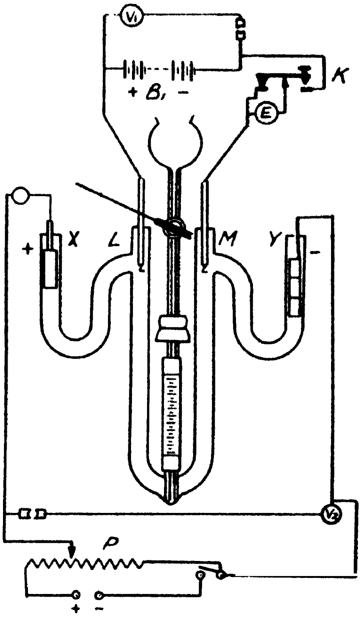

FIG. 31 (XVI³)
Apparatus of Price and Lewis

In order to maintain a constant potential gradient across the main U-tube (LM), the potential across the side-arms (XY) has to be adjusted at regular intervals (e.g. of 2 minutes) throughout a given determination. To effect this, a balance method is employed. A battery of secondary cells B, of constant E.M.F., which E.M.F. is measured by means of a high-resistance precision voltmeter V_1, is used as standard. This E.M.F. can have any convenient value. The potential across LM is adjusted at regular intervals so that it is equal in value to the standard chosen, by varying the potential across XY by use of the potentiometer P. The balance is obtained with the capillary electrometer E. As a consequence no current passes from LM. and the known constant potential gradient in the main U-tube is precisely maintained.

Each limb of the main U-tube is illuminated from the side by a separate narrow beam of intense light which enables a vertical cross-section of each interface to be clearly defined. The position of each interface is measured, on the scale attached to the tube, by means of a horizontal telescope which may be moved in any vertical plane.

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[1] *See*, for example, Dickinson, *Trans. Farad. Soc.*, 1940, *36*, 839; *ibid.*, 1941, *37*, 140; *ibid.*, 1944, *40*, 48; Growney, *ibid.*, 1941, *37*, 148.

[2] *Ibid.*, 1933, *29*, 775.

The tube is immersed in a thermostat with glass walls, the face of the thermostat between the scale and the telescope being optically plane. The movement of a boundary may be measured to within 0·25 mm.

The apparatus just described was used in the first instance by Price and Lewis in the determination of the electrophoretic mobility of aqueous lecithin dispersions diluted to 0·05 per cent concentration with citrate buffer with a maximum concentration of citrate ion (when the *p*H = about 5) of 0·01 N. It was considered that at such low concentration of the buffer the effect on the electrophoretic mobility of the lecithin dispersion would be very small. This conclusion was justified by reference to the results of Powis's investigations. Powis found that whereas the effect on the electrophoretic velocity of a negatively charged engine-room emulsion due to the presence of a uni-univalent salt, with a concentration of 0·01 N, was small, the effect of a salt with a univalent cation and a multivalent anion, at the above concentration, was even less. Price and Lewis suggested that the effect on an amphoteric substance like lecithin would be still less.

The overlying liquid was citrate buffer of the same ionic concentration as the dispersion. In harmony with the experiments of Northrop and Cullen it was found that the addition of 2 per cent of sucrose to the dispersion greatly facilitated the adjustment and maintenance of a sharp boundary without in any way affecting the mobility. The mean of the movements of the two boundaries (upwards in the anode limb, downwards in the cathode limb) during the 30-minute ' run ' was used in the final calculation.

In the use of the apparatus of Price and Lewis for the determination of the mobility of certain emulsion globules, Dickinson[1] used a supernatant liquid of the same ionic composition as the dispersion mixture, while to obtain a *p*H value of 4·0 the solutions were made N/10,000 with respect to hydrochloric acid. In order to obtain sharp boundaries, 2 per cent of A.R. sucrose was added to the emulsion. The same author[2] in investigating the effect of *p*H on the mobility of emulsions used *p*H values ranging from 2·0 to 11·8, while the cation concentration was maintained throughout at a value 0·01 N with respect to sodium ion. From *p*H 2·0 to *p*H 5·5 the desired *p*H was obtained by diluting 10 ml. of 0·1 N sodium chloride and the required amount of dilute hydrochloric acid with water, or stock emulsion, to 100 ml. Although these solutions were unbuffered, the *p*H values could usually be repeated to 0·03 of a *p*H unit. From *p*H 5·5 to *p*H 11·8 the desired *p*H was obtained by the use of either a phosphate or a borate buffer. The highest *p*H obtainable under the given conditions was that of 0·01 N caustic soda. The author found that when both phosphate and borate buffers were used, the mobilities agreed in the *p*H region covered by both of the buffers. As before, the supernatant liquid and the dispersion mixture were of the same ionic composition, and to obtain sharp boundaries 2 per cent of A.R. sucrose was added to the emulsion.

[1] *Trans. Farad. Soc.*, 1940, *36*, 839.
[2] *Ibid.*, 1941, *37*, 140.

Growney,[1] in an examination made of the effects produced by a variation in pH of the aqueous phase on the electrophoretic mobility of an emulsion in the presence of 0·01 N sodium chloride or other univalent salt, also employed an apparatus of the Price and Lewis type. Between pH 2 and pH 7 both the dispersion and the supernatant liquid contained 0·01 N sodium chloride, the pH being adjusted by the addition of suitable amounts of hydrochloric acid or (above pH 6) by sodium hydroxide. Above pH 7 it was found necessary to use a buffer (sodium diborate). To obtain clear boundaries the dispersion had to have a greater density than the supernatant liquid. In every case the dispersion contained 2 per cent of A.R. sucrose. For other improvements in design see Tiselius [2] (prevention of convection), Lamm [3] (more exact determination of the movements of the boundaries), Longsworth and MacInnes [4] (the making of more exact computations).

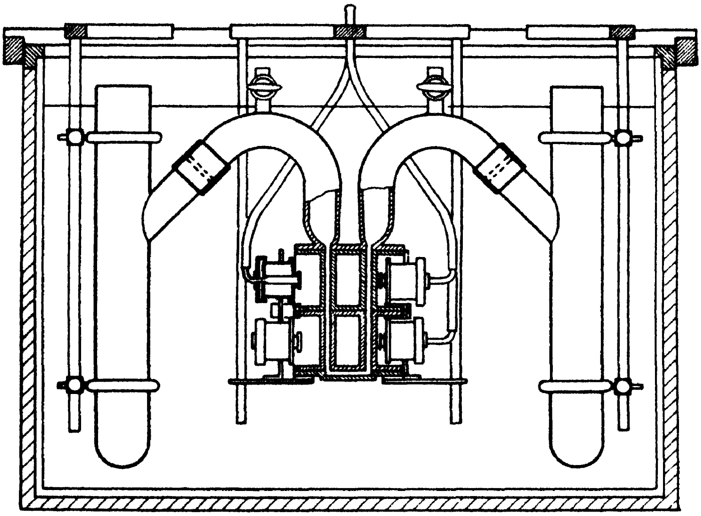

FIG. 32 (XVI³)
Tiselius U-tube electrophoresis cell

The Tiselius U-tube electrophoresis cell is illustrated in Fig. 32 (XVI³). The Tiselius cell is incorporated in the Hilger Electrophoresis Apparatus.[5] The optical method used is, in effect, an application of the Foucault and Töpler *schlieren* method to the limbs of the U-tube containing the preparation which is being subjected to electrophoresis.[6] Although this method is largely qualitative it may be made quantitative by an arrangement of crossed diaphragms or slits at conjugate image points. It is often used for electro-phoretic separations. The following features are partly responsible for the increased accuracy obtainable with the Hilger apparatus.

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[1] *Ibid.*, 1941, *37*, 148.

[2] *Ibid.*, 1937, *33*, 524.

[3] *Z. physik. Chem. A.*, 1928, *138*, 313; *ibid.*, 1929, *143*, 177.

[4] *J. Amer. Chem. Soc.*, 1940, *62*, 705.

[5] The authors are indebted to Dr. F. Twyman, F.R.S., and Messrs. Hilger Ltd., London, for details of the Electrophoresis apparatus based on the apparatus of Teselius made by them. A number of forms are described. The references to applications in the literature have also been provided. Reference Pamphlet, 1941, S.B. 293/2, Hilger Ltd.

[6] Svedberg and Pederson, *The Ultracentrifuge*, The Clarendon Press, Oxford, 1940; Tiselius, *Trans. Farad. Soc.*, 1937, *33*, 524; Svensoon, *Kolloid-Z.*, 1939, *87*, 181.

(*a*) Accurate collimation is obtained in the light which traverses the U-tube. This eliminates serious errors which arise when the light is convergent or divergent, owing to the vertical variation in the refraction gradient.

(*b*) The lenses used for this purpose, and for the subsequent focusing of the image of the first diaphragm upon the second adjustable diaphragm, are corrected for aberration as otherwise this would appear erroneously as a refraction gradient. This aberration correction is obtained by making one surface in each lens non-spherical.

(*c*) The objective used for the projection of the image of the U-tube has only two glass-to-air surfaces and thus avoids troublesome reflections which may affect the photographic image.

In operation, the slit-shaped diaphragm illuminated by light received from the light source (a sodium or mercury lamp) is imaged on a straight diaphragm by lenses of aperture 150 mm., a collimating lens being mounted upon the bar stand and viewing-lens on a tripod stand. The colloidal suspension upon which the test is to be made is contained in the U-formed cell suspended with the thermostat. The optical system of the camera projects upon the photographic plate a rectangular image corresponding to each U-tube limb, which it reproduces in its vertical dimension. In its horizontal dimension, however, owing to the use of a cylindrical lens in the system, the image plane is conjugate to the plane of the second diaphragm. This is adjustable for vertical position by a millimetre scale and for inclination by a degree scale, so that the profile of the refractive index gradient at some particular boundary within either limb is represented graphically on the plate and may be adjusted to lie within the dimensions of the photographic picture obtained, i.e. approximately 30 × 20 mm. This corresponds to each half-limb of the U-tube. Ordinarily the images of each complete limb overlap but shutters are provided so that alternate halves of the U-tube may be viewed and exposed for photography. When it is desired to view the patterns from both limbs simultaneously a double deviating prism may be supplied to cause the images to be separated. This is supplied in a cell which is arranged to be mountable easily inside the camera and to take up its adjustment automatically.

The standard form of cell or U-tube upon which the observations are made is of a special compound form in four sections. The two middle sections are identical in construction, having ground plates at either end by means of which they make contact with each other and with similar plates attached to the upper free end and the lower connecting section. The internal dimensions of the two middle operative sections are each 46 mm. in height and 25 × 3 mm. cross-section. Other forms of U-tube have been made for special purposes.

The two middle sections may be displaced laterally with respect to one another, and with respect to the upper and lower sections, by means of a pneumatic motion fitted to the mounting. In this way the formation of the initial boundary between the buffer and solution under investigation is facilitated and, at the end of the experiment, sectioning prevents the mixing of electrophoretically separated components. It is then possible to remove the apparatus from the water-bath and pipette out the contents of each compartment separately.

The U-tube is connected to two electrode vessels containing reversible silver-silver chloride electrodes and having a capacity of about 500 ml. Larger vessels with a capacity of about 2,000 ml. may also be supplied and are required if the difference in electrophoretic mobility of the substances to be separated is small. The U-tube and electrode vessels are held in the same metal stand by which they are suspended in the thermostat water bath. This is maintained at a temperature only slightly above zero centigrade by means of a refrigerator and thermostatically controlled circuit. By the procedure of Tiselius this ensures that the temperature within the U-tube shall be approximately that of the maximum density of the solution, convectional disturbances then being reduced to a minimum.

One of the electrode vessels may be fitted with a compensator consisting of a plunger with a clockwork motion by means of which a movement of the colloidal solution as a whole in the U-tube may be set up in opposition to the direction of migration of some particular molecular species which it is desired to separate from another having only slightly different migration velocity.

Micro-Apparatus. A micro-form of the Hilger Electrophoresis Apparatus is also available, capacity 0·9 ml. per limb-section, total capacity of lower half of U-tube 2·0 ml. The medium-capacity form, based upon the above apparatus, may readily be converted to the micro-form when only small quantities of the test sample are available for electrophoretic analysis.

This form employs a four-section U-tube similar to the medium-capacity tube, but of smaller capacity, viz. 0·9 ml. for each limb-section. This tube may be mounted for the purpose of the test in the same U-tube frame as is used for the medium-size tube, thereby saving the additional expense of a special holder. In cases where the apparatus is required to be continuously in action, the possession of a second holder may, however, be an added convenience, and the holder for this purpose is therefore listed separately. The optical arrangements for the above micro-form U-tube remain the same as those used with the medium-capacity tube.

Larger Type. The standard size of U-tube takes about 10 ml. of material which, although generally adequate, imposes limitations upon the quantity that can be dealt with when the process is required to be used for the large scale separation of pure components. These limitations have resulted in the development of an apparatus capable of dealing with a greater quantity and using a U-tube with a capacity of about 150 ml. The U-tubes of this size are made with four middle sections and are immersed in a water-bath whose windows, as well as the viewing-lens provided in the outfit, are sufficiently large to enable observation to be made upon them all simultaneously during electrophoresis. U-tubes of these dimensions require a special form of mechanical support and larger electrode vessels are also required. These cannot be accommodated in the water-bath on account of their size but are mounted externally on separate stands. The procedure of examination of the electrophoretic pattern is as for the medium size described above but, on account of the different dimensions of apparatus, special optical arrangements need to be made.

As the normal size of U-tube would still be required to be used for mobility determinations and to provide greater accuracy than is otherwise possible, it would appear that two independent sets of apparatus would be needed in laboratories interested in large-scale work. This situation may, however, be met, generally, by the use of convertible apparatus capable of being used for either large- or medium-capacity work. The Hilger Convertible Electrophoresis Apparatus enables conversion to be made from medium-to large-capacity operations merely by minor adjustments to the optical system and the necessary interchange of the U-tubes in their mounts. This form of the Electrophoresis Apparatus is therefore capable of serving a double purpose. It can be used (*a*) for accurate electrophoretic tests on samples and the determination of electrophoretic mobility, of their homogeneous components, and also for (*b*) the electrophoretic fractionation of relatively large quantities.

In the use of the convertible apparatus the only change when the apparatus is used for medium capacity, by comparison with the standard system, is in the use of a lens of aperture 220 mm. to take the place of the collimating lens there used. When the apparatus is used for large capacity operations the viewing lens is removed and the position of the camera is readjusted along the bar.

The direct current supply to the electrodes is obtained from a rectifier giving 1,500 volts maximum with continuous adjustment from 10 ma. to 250 ma.

Light Sources. The above apparatus may be used with either a sodium lamp or preferably mercury vapour lamp.

Slit Diaphragms. It has been demonstrated by Svensson [1] that if in the Electrophoresis Apparatus narrow slits are used in conjugate focal positions instead of the straight knife-edge diaphragms, the electrophoretic pattern is obtained as a bright line on a dark ground. This is an advantage in some respects although the line is not of uniform thickness on account of the varying gradient. By giving the second slit a tapered end this defect has in some measure been overcome, at least for one peak at a time for which appropriate adjustment can be made expressly.

Applications of Tiselius Electrophoresis Technique.[2] Tiselius,[3] applied the electrophoresis apparatus to an analysis of the serum proteins, showing that it was not only possible to separate serum albumin from serum globulin, but that in normal horse and rabbit serum the globulin is not a single substance but consists of α, β, and γ components. Tiselius and Kabat [4] showed that antipneumococcal horse serum contains a new globulin component not present in normal horse serum and specifically precipitable by the type-specific polysaccharide.

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[1] *Kolloid Z.*, 1939 ,*87*, 181.

[2] These references are from Hilger Pamphlet, 1941, 293/2.

[3] *Biochem. J.*, 1937, *31*, 1464.

[4] *J. of Exper. Med.*, 1939, *69*, 119.

Normal human serum, investigated by Stenhagen,[1] was demonstrated to have a similar electrophoretic constitution to normal rabbit and horse serum. Each of these researches employed the simple Töpler *schlieren* optical method.

By the application of optical methods of modified form, the quantitative composition of normal human serum was shown by Kekwick,[2] Longsworth *et al.*,[3] and Svensson to exhibit only slight fluctuations. In pathological conditions such as myeloma, nephritis, and pneumonia, however, marked changes occur in the protein constitution of human serum (Blix; [4] Longsworth and MacInnes [5]).

Pedersen and Waldenström [6] have shown that the bilirubin present in normal and pathological serum migrates electrophoretically with the albumin but it may be displaced (Stenhagen and Theorell [7]) from combination by the addition of nucleic acid, after which it is possible to isolate, by electrophoresis, non-pigmented serum albumin. Luetscher [8] has found under certain conditions that serum albumin consists of two components, the amounts of these being changed in sera from pathological subjects.

In the field of enzyme chemistry the electrophoretic method has met with success. Using a special form of apparatus Theorell [9] was able to isolate the yellow respiratory enzyme of Warburg from extracts of beast cells. With this apparatus Agner [10] has carried out experiments on horse liver catalase and has isolated from it a copper-protein compound. Several investigators (Tiselius *et al.*,[11] Ågren and Hammarsten,[12] Herriot, Desreux, and Northrop [13]) in experiments on crystalline pepsin have found that the activity is associated with a protein which is negatively charged even in extremely acid solutions. The crystals also contain non-protein nitrogenous constituents of low mobility.

An interesting study by Tiselius and Eriksson-Quensel [14] on the degradation of ovalbumin by crystalline pepsin reveals facts of importance with regard to protein structure. One form of degradation product alone was observed, unchanged ovalbumin being present in addition.

The formation of new types of molecules in mixtures of the hemocyanin respiratory pigments from different species has been demonstrated electrophoretically by Tiselius and Horsfall.[15]

The electrophoretic method is being applied in the study of viruses; the crystalline virus causing bushy stunt disease of tomato plants behaves as a homogeneous protein (McFarlane and Kekwick [16]). Suspensions of vaccinia virus have a characteristic electrophoretic behaviour (McFarlane [17]).

The lactogenic hormone of the pituitary gland has been the subject of investigation (Shipley *et al.*[18]; Lui *et al.*[19]). These workers have demonstrated its electrophoretic homogeneity. The protein constituents of milk whey have been examined by Mellander.[1]

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[1] *Biochem. J.*, 1938, *32*, 714.
[2] *Ibid.*, 1939, *33*, 1122.
[3] *J. Exper. Med.*, 1939, *70*, 399.
[4] *Z. für die gesamte Experimentelle Medizin*, 1939, *105*, 595.
[5] *J. Exp. Med.*, 1940, *71*, 77.
[6] *Z. für Phys. Chem.*, 1937, *245*, 152.
[7] *Trans. Farad. Soc.*, 1939, *35*, 743.
[8] *J. Amer. Chem. Soc.* 1939, *61*, 2888.
[9] *Biochem. Z.*, 1934, *272*, 155.
[10] *Biochem. J.*, 1938, *32*, 1702.
[11] *Ibid.*, 1938, *32*, 1814.
[12] *Enzymologia*, 1937, *4*, 49.
[13] *J. of Gen. Phys.*, 1940, *23*, 439.
[14] *Biochem. J.*, 1939, *33*, 1752.
[15] *J. Exper. Med.*, 1939, *69*, 83.
[16] *Biochem. J.*, 1938, *32*, 1607.
[17] *Trans. Farad. Soc.*, 1940, *36*, 257.
[18] *J. Exper. Med.*, 1939, *69*, 785.
[19] *J. Gen. Phys.*, 1940, *23*, 433.

The previously quoted papers have dealt with protein material entirely, but applications of the method may be found for polysaccharides. The isolation of a polysaccharide as well as the protein tuberculin, from the culture filtrate of tubercle bacilli by Seibert, Pedersen, and Tiselius [2] serves as an example. Mayer and Chaffee [3] have used the method to demonstrate the presence of hyaluronic acid in pleural exudate and in solution.

Developments in Electrophoresis. According to Tiselius [4] improvements which form a basis for developments in electrophoresis are chiefly as follows :

(1) Increasing the potential gradient in the electrophoresis tube without causing undesirable heat convections. This is one of the most difficult problems in electrophoresis, especially with dilute solutions, as the boundaries in the electrophoresis tube are easily destroyed by such convections. The size and shape of the tube must be arranged to give proper cooling—the apparatus naturally being immersed in a water thermostat—and also to have as small temperature gradients as possible within the tube. A particularly effective means of diminishing the risk of heat convection currents is to choose a working temperature of about + 4°, that is in the region of maximum density of water where the variation of density with temperature is very small. Many substances to be investigated are reasonably stable only at low temperature and + 4° it is now used in most electrophoresis work.

(2) Arrangements for taking out samples of the solution in the electrophoresis tube after concluding the experiment in order to obtain the fractions which have been separated or to determine the rate of migration by analysis.

(3) Avoidance of disturbances produced by the electrostatic processes at the electrodes by using reversible electrodes and interposing a large volume of buffer solutions between the electrodes and the electrophoresis tube.

(4) Use of more accurate optical observation methods.[5, 6]

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[1] *Biochem. Z.*, 1939, *300*, 240.

[2] *J. Exp. Med.*, 1938, *68*, 413.

[3] *J. Bio. Chem.*, 1940, *33*, 83.

[4] International Congress of Pyre and Applied Chem., 1947. Published as a Supplement to *Chem. and Ind.*, 1948, *9*.

[5] *Loc. cit.*

[6] Svensson, ' Electrophoresis by the Moving Boundary Method. Dissertation Uppsala, 1946 ', *Arkiv för Kemi*, XXIII(A), No. 10, 1946.

CHAPTER XVII [3]

HIGH VACUUM TECHNIQUE [1]

SECTION 1: VACUUM PUMPS

IN the high-vacuum pumping systems now usually employed, the pressure is first reduced from atmospheric to about 0·1 mm. of mercury (760 mm. mercury = 1 atm.) by means of a mechanical pump, generally of the rotary oil-sealed type. The further reduction from this ' fore-vacuum ' or ' backing ' pressure down to a still lower pressure, such as 10^{-4} or 10^{-6} mm. mercury, is achieved by means of a condensation pump.[2]

The production of a high vacuum in a vessel consists essentially of the removal from the vessel of a proportion of the gas and vapour molecules which may be present. It is interesting to note that the number of molecules in the standard atmosphere (760 mm. mercury and 0° C.) is about 3×10^{19} per ml., each molecule having an effective diameter of about 3×10^{-8} cm. and travelling, on the average, about 10^{-5} cm. between collisions with other molecules.[3] If, by means of a vacuum pumping system, we remove some of the air molecules from a vessel originally containing them at atmospheric pressure, and ultimately achieve the relatively very low pressure of 10^{-6} mm. mercury (i.e. of the order of 10^{-9} atmosphere) there would still remain about 4×10^{10} molecules per cc., but the average distance the molecules travel between successive collisions, or their mean free path, would now be approaching 10^{-4} cm. Under these conditions, therefore, the probability of collisions occurring between individual molecules is small compared with collisions between the molecules and the walls of the containing-vessel, provided of course that the dimension of the vessel lies within suitable limits. It will be appreciated that, fundamentally, the production and maintenance of high vacua are means whereby to increase the mean free path of gas (or vapour) molecules within a container, and so reduce the tendency for either inter-molecular collisions to occur, or collisions between gas molecules and, for example, electrons, or other particles of an atomic nature.

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[1] This chapter amplifies the chapter on pumps in Vol. I. It has been written by Mr. G. Burrows and is based on a paper by him in the *J. Sci. Inst.*, 1943, *20*, 21, and includes an additional discussion on certain practical features and items of equipment. The authors wish to express their indebtedness to Mr. G. Burrows for this assistance and to Sir Arthur P. M. Fleming, C.B.E., D.Eng., Director of Research and Education, Metropolitan-Vickers Electrical Co. Ltd., Manchester, who gave permission for the work to be undertaken. Thanks are also due to the Editor of the Institute of Physics for use of a number of blocks from the *Journal of Scientific Instruments*.

[2] *See* Vol. I, Chap. VII. It is intended in the next edition to incorporate this new chap. in Vol. I. Subsequent chapters will also be connected with the appropriate sections in Vols. I and II (5th edition).

[3] Kaye and Laby, *Physical and Chemical Constants*, Longmans, Green & Co., 9th ed., 1941, 42.

Various text-books and articles have been published dealing with high-vacuum technique, and the reader is recommended to consult these [1] should he wish to supplement his knowledge with further and more detailed descriptions of the apparatus involved and of principles of operation.

The pumps considered here are those types generally employed in the production of high vacua for laboratory use and have been outlined in Vol. I, namely, the rotary oil-sealed type and the condensation pump. Other kinds of vacuum pumps are, of course, available, such as the piston pumps described in Vol. 1 (p. 243) or the molecular pumps (Vol. I, pp. 250–1), but these are not capable of such general application as the types now to be described.

Rotary Oil-Sealed Pumps

This type of pump usually embodies a rotating member which, by means of vanes or an eccentric motion, compresses and ejects the gas and/or vapour through an oil-immersed non-return outlet valve. A number of these will be described.

The 'Metrovac' [2] series of rotary vacuum pumps include the type S.R.2, the type D.R.1, and the type S.R.5.

The Type S.R.2 Pump is a single-stage, oil-immersed vane type rotary pump of simple construction with few working parts. In the event of the pump becoming contaminated internally, due to the pumping of substances tending to cause corrosion, it can be dismantled readily for inspection and cleaning if necessary.

Specification :

Power input	⅛ h.p.
Speed of rotation	350 r.p.m.
Displacement	½ cu. ft./min.
Pumping speed, at 0·1 mm. mercury	130 ml./sec.
Limiting pressure	0·020 mm. mercury
Amount of oil required	1,250 c.c.

The S.R.2 pump may be used as a backing-pump for small condensation pumps, it being particularly suited for backing the type '02' 'Metrovac' oil-condensation pump.

The Type D.R.1 'Metrovac' pump has two stages in series. Fig. 1 (XVII³) shows an outline drawing of this pump. The driving shaft is direct coupled by flexible coupling (C) to a standard ¼ h.p. 1,450 r.p.m. motor (M), a helical-geared reduction drive being incorporated within the pump (P) itself. The pump and motor are mounted together on a cast bedplate (S).

The method of drive has the advantage of great reliability; unlike a belt drive it is unaffected by accidental splashing of oil, and does not require adjustment.

The pump itself is well balanced, as the vanes of the two stages are arranged at right angles. In general very little vibration is set up when the pump is running, which is often an important point when it is required for laboratory purposes. The design is such that there is little outlet valve noise, and this, together with the use of helical gearing (which is enclosed in an evacuated space between the two stages of the pump), ensures quiet running.

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[1] *See* 'Guide to Further Reading', Vol. I.

[2] Registered trade mark of the manufacturers, Metropolitan-Vickers Electrical Co. Ltd.

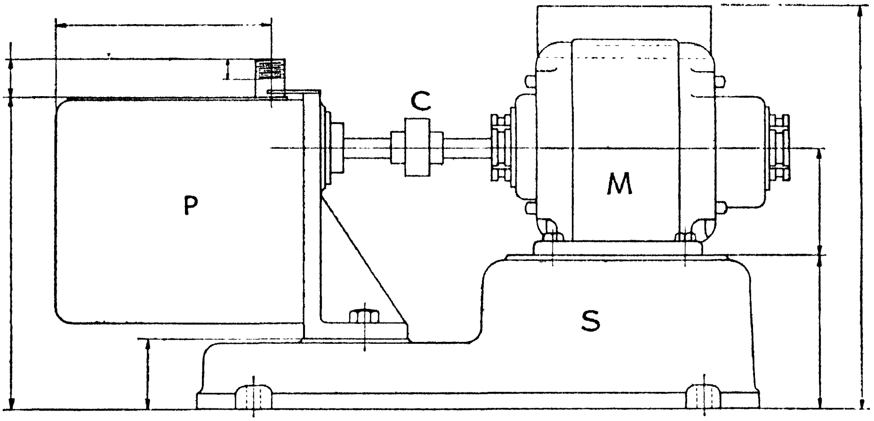

FIG. 1 (XVII^3)
Type D.R.1. ' Metrovac ' two-stage rotary vacuum pump

Specification :

Power input	¼ h.p.
Displacement	2 cu. ft./min.
Pumping speed at 0·5 mm. mercury	800 ml./sec.
,, ,, ,, 0·1 ,, ,,	670 ,,
,, ,, ,, 0·02 ,, ,,	320 ,,
Limiting pressure . . .	Less than 0·01 mm. (measured by Pirani Gauge)
Amount of oil required . . .	2,700 c.c.

The Type S.R.5 ' Metrovac ' pump is a single-stage, oil-immersed, vane-type rotary pump of simple construction. It can be ' Texrope ' driven from a motor mounted in common with the pump on a cast iron bedplate. The starting equipment for the motor can, if required, be included in this unit arrangement.

Specification :

Power input	3 h.p.
Speed of rotation	450 r.p.m.
Displacement	40 cu. ft./min.
Limiting pressure	0·025 mm. mercury

Various modifications of this pump are available for use under abnormal conditions. For example, when contaminating vapours are present, arrangements can be made for feeding a continuous supply of fresh clean oil to the pump interior.

The ' Kinney ' [1] high-vacuum pump is of the oil-sealed rotating-plunger type and is shown in cross-section in Fig. 2 (XVII^3).

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[1] Manufactured for the European market by General Engineering Co. (Radcliffe), Ltd., Radcliffe, Lancashire, under licence from the Kinney Manufacturing Co., Boston, Mass., U.S.A.

In operation, as the shaft 9 rotates in the direction indicated by the arrow, carrying the rotary cam 8 round with it, a rotary plunger motion is imparted to the piston 5 tangent to the inside of the cylinder. This motion tends to create a vacuum behind the piston and draws in air through the hollow slide and at the same time the air in front of the piston is forced out through the discharge valve 46 and nozzle 50 into a separator tank, thence to the atmosphere. Just before the piston attains its highest position, the slots in the hollow slide (through which air is drawn from the hollow slide into the cylinder) are completely closed by the slide pin 7, thus forming an effective mechanically operated suction valve. Oil is discharged from the pump along with the air into an oil separator of sufficient capacity to allow any condensed moisture to settle out, after which the oil is used over again, this process being continuous and automatic. Various sizes of Kinney high-vacuum pumps are available ranging from a pump having a displacement of 12 cu. ft. per minute and requiring a ½-h.p. motor up to a pump having a displacement of 680 cu. ft. per minute and requiring a 35-h.p. motor.

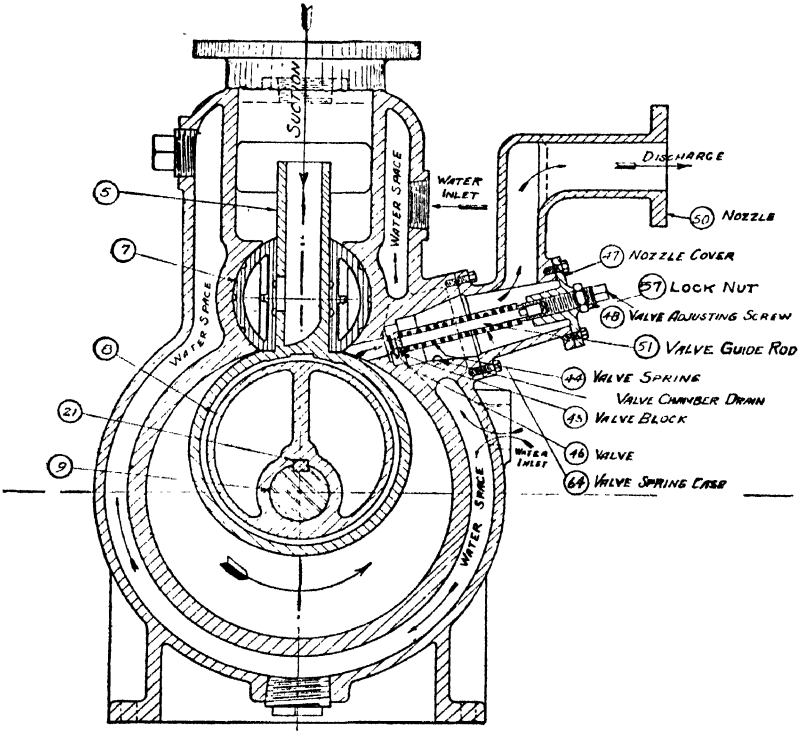

FIG. 2 (XVII^3)
Cross-section through typical 'Kinney' high-vacuum pump

The Stokes[1] oil-sealed rotary-plunger pump incorporates a built-in oil clarifier, which is recommended for installations where water vapour may reach the pump. The Stokes oil clarifier is a high-speed centrifugal separator that automatically removes not only water but also foreign matter from the oil. The clarifier is so arranged that the dirt removed from the oil, and collected in the bowl, may readily be cleaned out. Emulsified water is automatically separated and discharged.

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[1] Stokes Machine Co., Philadelphia, Pa., U.S.A. (W. Edwards & Co., London, S.E.5).

General Remarks

When considering the use of a mechanical backing pump in conjunction with a condensation pump, impurities such as water vapour, and other fluids in the vapour phase, which would be frozen or liquefied in the cold trap preceding a mercury condensation pump, must be handled by the mechanical backing pump when no cold trap is used. The last-named condition usually applies to oil-condensation pumps. But water vapour and certain other vapours are condensed to liquid on the exhaust side of the rotary backing pump, giving rise to contamination of the sealing oil and corrosion of the internal parts. It is recommended, therefore, that a vacuum-tight container holding phosphorus pentoxide be inserted in the pipe-line between the oil-condensation pump and the backing pump, in order to trap the water vapour before it reaches the mechanical pump. The container should be provided with a glass window and a detachable cover, so that the condition of the pentoxide may be observed, and renewal effected when necessary.

Where there is a large proportion of condensable vapours to be handled, as in distillation work, the phosphorus pentoxide becomes fouled relatively quickly. In such circumstances it will probably be found necessary periodically to drain the mechanical pump and recharge with fresh oil, or to arrange that the pump is provided with a constant flow of fresh sealing oil. Various other expedients may be used to reduce the harmful effects of the condensation of contaminating vapours in the sealing oil of mechanical backing pumps. Such pumps may themselves be backed by a smaller mechanical pump working at a relatively higher pressure; most of the condensation and consequent corrosion then occurs in the smaller pump thus reducing the maintenance and running costs. Or a steam coil may be immersed in the sealing oil in order to raise the temperature of the oil and so prevent condensation occurring. Water vapour may be removed by means of a centrifugal clarifier through which the sealing oil is circulated. Both water and other vapours may be segregated and isolated on the exhaust side of the pump by means of a solvent trap.[1]

Another point to be remembered in connexion with rotary oil-sealed vacuum pumps is that their speed becomes zero at their lowest limiting pressure. Thus the claim sometimes put forward that such-and-such a rotary pump will get down to a pressure as low as 0·001 mm. of mercury is of little value in practice, as the pump has no pumping speed at this value of pressure, if it is the lowest that the pump will achieve. What is really required is the actual pumping speed over a range of pressures, but this information is not always readily available. Moreover, the pressure of 0·001 mm. of mercury may have been measured with a McLeod type of gauge which measures only the permanent gas pressure, and takes no account of condensable vapours which may be present, such as, for example, in the sealing oil of the rotary pump.

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[1] Askew and Bourdillon, *J. Sci., Inst.*, 1932, *9*, 280. A detailed description of this device is given in *Physico-Chemical Methods*, Vol. I, p. 261.

If pressures of the order of 0·001 mm. of mercury or less are required, the use of an oil-condensation pump is indicated, since this type of pump, according to the design selected, can maintain its rated speed at a relatively constant value over an appreciable proportion of the pressure range 10^{-3} mm. to 10^{-7} mm. of mercury.

Condensation Pumps

Condensation pumps may be divided into two main classes, those which use (*a*) mercury as the working liquid, and those which use (*b*) low vapour pressure organic liquids such as 'Apiezon' oils or the esters of certain organic acids, for convenience referred to as oil-condensation pumps.

Condensation pumps are actuated by the evaporation of a liquid, the resultant vapour passing through a jet, the vapour thereafter being condensed and returned to the pump boiler. This method of operating a vacuum pump was suggested by Langmuir[1] in 1916, the liquid chosen being mercury. A mercury-condensation pump, if suitably backed, will achieve a limiting low pressure on its suction side of 0·001 mm. mercury, this value being the vapour pressure of mercury at the temperature of the cooling water of the pump, assuming that the water is at room temperature.

Mercury-Condensation Pumps

Various types of mercury-condensation pumps are illustrated in *Physico-Chemical Methods*, Vol. I, pp. 253–5.

A new type of condensation pump of high speed in which the evaporation of mercury is very small has been described by Bull.[2] This pump is shown in the lower part of Fig. 3 (XVII³). In it mercury is evaporated from the boiler A and passes through a wide connecting tube into the glass jet P. This jet is of an annular construction in order that the space through which gases can diffuse into the mercury vapour is as large as possible for a given rate of expenditure of energy in boiling mercury. The hollow vapour jet passes into an annular space of which both the inner D and the outer surface C are water cooled. The condensed mercury and the expelled gases leave the pump by the water-cooled return tube E, the mercury going to the boiler A and the gases to the fore-vacuum reservoir U. Leading dimensions can be recognized from the scale on Fig. 3 (XVII³).

The pump distils only negligible quantities of mercury vapour against the jet, and the speed is found to be so high that the resistance to pumping due to known forms of mercury trap and of taps constitute the major limitation on the pumping speed available.

M. Knudsen[3] has shown that there is a critical temperature, at about – 140° C., below which every mercury atom impinging on a glass surface is caught. Above this temperature the mercury atoms may be reflected in any direction after impact on the glass. The type of mercury trap using long re-entrant tubes immersed in liquid air ensures that no atom of mercury can possibly escape, but it adds greatly to the length of the path through which the gases must diffuse. The result is that very good vacuum can be obtained, but the speed of the trap is very low. Other traps, in which the resistance to diffusion is much less, permit a small fraction of the mercury molecules coming up from the pump to escape by rebounding several times from the uncooled surfaces without touching the cooled surface. When using these traps it is found that the residual pressure in the vacuum vessel is a function of the mercury-vapour pressure at the pump, and a compromise has to be made, appropriate to the conditions required, between the residual pressure of mercury vapour and the speed of pumping.

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[1] Langmuir, *Gen. Elect. Rev.*, 1916, *19*, 1060.

[2] B.P. 552898–1941.

[3] Knudsen, M., *Ann. Physik.*, 1916, *50*, 472.

A design of an improved mercury trap, and a tap which enables the pump to be used more efficiently, will now be described.[1]

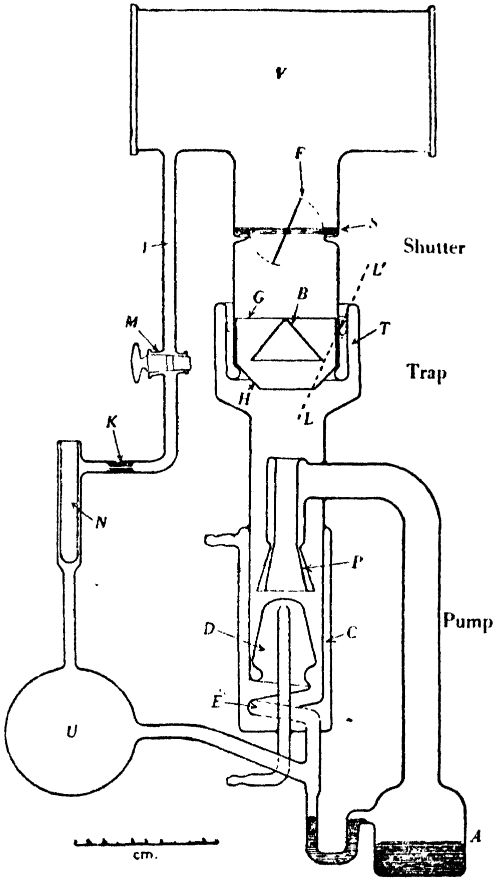

FIG. 3 (XVII^3)
High-speed diffusion pump trap and shutter

In the new trap every mercury atom evaporating from the pump must impinge on the cooled surface of the trap, while at the same time the obstruction to the diffusion of gases is very small, perhaps even lower than that of the pump itself. One method of constructing this trap is shown in the middle part of Fig. 3 (XVII^3). In this, a metal cylinder G is in heat contact with the liquid air-cooled glass sleeve T. The truncated metal cone H resting on the lip of the cooled sleeve takes up the same temperature as the cylinder part through metallic conduction. The shield B, which need not be at a low temperature, is suspended by wires or short rods inside the cylinder G. A mercury molecule emerging from the pump impinges either directly upon the cooled surface or reaches it after one or several reflections from the shield. The diameter of the shield has to be large enough for an interception of all molecules passing through the aperture of H and travelling along tracks which are so steep that they would miss the cooled concave surface of G. A limiting path of the greatest slope admitted is indicated in Fig. 3 (XVII^3) by the broken line L′–L connecting the smallest aperture of H with the largest aperture of B. The trap may be made from any material which does not amalgamate ; for instance, from stainless steel. Also traps made completely out of glass are suitable. The shield of the glass trap is made conveniently from a flat circular glass plate suspended from the top.

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[1] Bull and Klemperer, *J. Sci. Inst.*, 1943, *20*, 179.

The new type of tap is a shutter shown in the top part of Fig. 3 (XVII³). Its function is to cut off the migration of mercury-vapour molecules into the vacuum vessel when the diffusion pump and trap are not in use.[1] It consists of a circular disk or flap F which can be rested on or lifted from an annular metal seating S which rests tightly on a constriction of the glass wall. The shutter is not greased. If magnetic shielding of an experimental tube is required, the shutter can be made from Mu-metal, thus forming a part of a Mu-metal cage surrounding the vessel V completely.[2]

Low-Vapour Pressure Liquids

(*The use of liquids other than mercury in condensation pumps is discussed in Vol. I,* pp. 256–60.)

Hickman has shown that the esters of certain organic acids possess, at room temperature, vapour pressures sufficiently low to enable them to be used as operating liquids in condensation pumps. Certain of these esters are now available commercially,[3] their properties being listed below:

Name	Chemical formula	Ultimate vacuum attainable with fractionating pump at 25° C.	Boiling point at 10^{-2} mm.
Butyl Phthalate	$C_6H_4(COOC_4H_9)_2$	10^{-4}	85° C.
Amoil . . .	$C_6H_4(COOC_5H_{11})_2$	$2{\cdot}5 \times 10^{-5}$	100° C.
Amoil-S . . .	$C_8H_{16}(COOC_5H_{11})_2$	$3{\cdot}1 \times 10^{-6}$	111° C.
Octoil . . .	$C_6H_4(COOC_8H_{17})_2$	$2{\cdot}5 \times 10^{-7}$	122·5° C.
Octoil-S . . .	$C_8H_{16}(COOC_8H_{17})$	5×10^{-8}	143·4° C.

More recently, organo-silicon oxide polymers known as silicone liquids have been developed and specially prepared for use in condensation pumps,[4] and it is claimed that, compared with other pump oils, they are less likely to decompose and oxidize under severe operating conditions.

Dow Corning[5] silicone fluids suitable for use in condensation pumps possess the following characteristics:

	Molecular weight	Boiling-point at 10^{-2} mm.
Fluid D.C. 702	530	160° C.
Fluid D.C. 703	570	200° C.

Oil-Condensation Pumps

A typical form of oil-condensation pump is shown in Fig. 4 (XVII³). The inlet end 3 of the pump is connected to the apparatus under evacuation.

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[1] Diagram from *J. Sci. Inst.*, 1943, *20*, 179.

[2] *J. Frank. Inst.*, 1936, *221*, 215, 383.

[3] Marketed by Distillation Products Inc., Rochester, New York, U.S.A.

[4] Brown, G. P., *Rev. Sci. Inst.*, 1945, *16*, 316.

[5] Dow Corning Corp., Midland, Michigan, U.S.A.

The gas diffuses into the vapour stream from the cowl 4, and thence is swept towards the outlet branch 5, which is connected to a suitable backing pump. Baffles 1 and 2 are situated in the mouth of the pump, the baffles being proportioned so as to reduce to a minimum the number of vapour molecules which may pass in an upward direction into the system under exhaust. Molecules having such motion are produced by multiple collisions in the vapour blast.

Where permanent gases are being handled, the type of condensation pump shown in Fig. 4 (XVII³) meets most normal requirements. Where, however, condensable vapours have to be pumped, as in molecular distillation processes, it is desirable to introduce certain modifications.

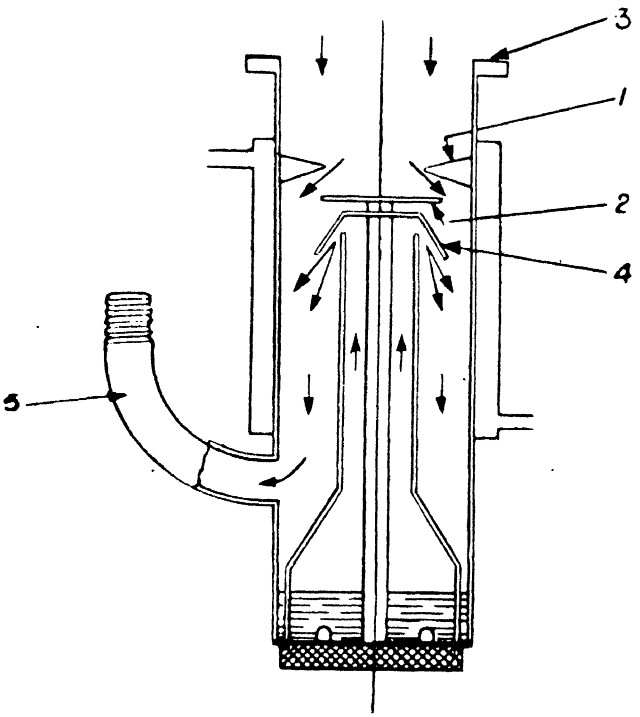

FIG. 4 (XVII³)
Cross-section through typical oil-condensation pump

Vapours which condense and dissolve in the pump fluid increase the total vapour pressure of the pumping liquid. Since the lowest pressure attainable by a condensation pump is determined by the total vapour pressure of the constituents of the pumping fluid, the presence of organic vapours of comparatively high volatility will, in general, impair the ultimate vacuum attainable by the pump. In order to assist in the elimination of volatile impurities into the fore vacuum, the outlet pipe, 5 (Fig. 4 XVII³), can be kept hot, the pipe being led into a vertical water-cooled condensing tube. The condensable vapours liquefy and are trapped in the bottom of the tube.

Another method proposed by Hickman[1] consists of a pump provided with separate boilers arranged so that the condensate from the fine pump, instead of returning directly to its own boiler, is first led to an external boiler. Here the more volatile components are separated out before the condensate from the fine pump is returned to its own boiler.

A pump which embodies the principle of separating the more volatile constituents of the operating liquid is now known as a fractionating condensation pump. These volatile components may be present as impurities which are produced by thermal decomposition of the operating liquid, or they may enter the pump in the form of vapours from the system under exhaust and dissolve in the pump liquid.

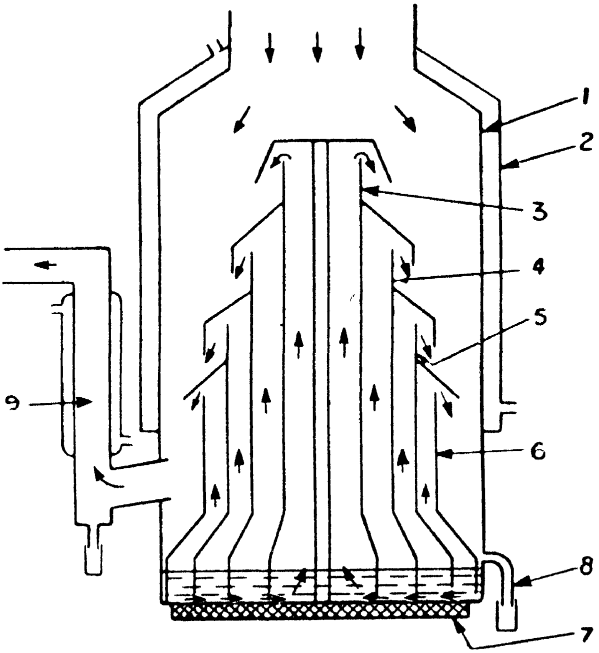

FIG. 5 (XVII^3)
Cross-section through fractionating oil-condensation pump

One form of fractionating condensation pump is shown in Fig. 5 (XVII^3). Essentially, the principle of operation of this type of pump is similar to the ordinary condensation pump previously illustrated (Fig. 4 (XVII^3)). The fractionating pump, however, embodies several important constructional differences which are introduced in order to enable the separation of the more volatile constituents to be effected. Referring to Fig. 5 (XVII^3) the working fluid of low vapour pressure contained in the base of the pump is heated by the heater 7. A number of concentric uptake tubes is provided, these being indicated at 3, 4, 5, and 6. Each of the tubes is fitted with a cowl so as to form a series of jets. The lower ends of the uptake tubes dip into the working liquid, but terminate a short distance from the floor of the boiler. Thus the working fluid is divided into several sections which communicate with one another through small openings adjacent to the floor of the boiler. When evaporation of the working fluid commences, the more volatile constituents boil off first, and, after being condensed on the cooled wall 1 of the pump, these tend to concentrate in the outermost annular compartment of the boiler formed by the lower ends of the uptake tubes 5 and 6. Constituents of lesser volatility tend to migrate, through the spaces beneath the lower edges of the uptake tubes, towards the centre of the pump. The least-volatile vapours are therefore used most effectively, that is, they feed the uptake pipe 3, which supplies the primary jet at the high-vacuum end of the pump. The intermediate annular compartments of the boiler, together with their respective jets, are fed with vapours which are graded as regards their volatility. An additional external condenser is shown at 9, and an overflow pipe at 8.

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[1] Hickman, *J. Frank. Inst.*, 1936, *221*, 215.

The ‘ Metrovac ’ [1] series of oil-condensation pumps are designed to work with Apiezon low-vapour-pressure oils as the working liquids. The bodies and the water jackets of the types 02, 03, and 03B pumps are constructed from a non-corrodible alloy, while the oil reservoir below is made of copper to provide high heat conductivity. For boiling the oil, the pumps employ specially designed heating elements having a long working life ; each is fitted by means of a single bayonet clip and may thus be replaced easily. The heaters can be wound for any one supply between 110 and 250 volts.

Various forms of vacuum connexion can be supplied, depending on the service for which the pump is intended.

Type 02 ‘ Metrovac ’ Oil-Condensation Pump (Fig. 6 (XVII^3))

Specification :

Type of oil	Apiezon ‘ A ’
Volume of oil	50 ml.
Limiting pressure	10^{-5} mm. mercury when using Apiezon ‘ A ’ Oil
Speed	6 litres/sec. at pressures below 10^{-2} mm. mercury on the high vacuum side
Highest permissible backing pressure	0·3 mm. mercury
Power consumption	450 watts

Type 03 ‘ Metrovac ’ Oil-Condensation Pump

Specification :

Type of oil	Apiezon ‘ B ’
Volume of oil	75 ml.
Limiting pressure	Below 10^{-6} mm. mercury
Speed	20 litres/sec. at pressures below 10^{-3} mm. mercury on the high vacuum side
Highest permissible backing pressure	0·05 mm. mercury
Power consumption	275 watts

For a variety of applications it is found that the type 02 pump is highly suitable for backing the type 03 pump, the 02 pump in turn being backed by a rotary pump such as the ‘ Metrovac ’ type SR2 or DR1, depending on the amount of gas being handled.

[1] Metropolitan-Vickers Electrical Co. Ltd., Manchester.

Type 03B ‘ Metrovac ’ Oil-Condensation Pump (Fig. 7 (XVII^{3}))

The type 03B which, while being similar in external appearance to the type 03 pump, combines the main characteristics of the 03 and 02 pumps.

Specification :

Type of oil	Apiezon ‘ B ’
Volume of oil	75 ml.
Limiting pressure	Below 10^{-6} mm. mercury
Speed	30 litres/sec. at pressures below 10^{-3} mm. mercury on the high vacuum side
Highest permissible backing pressure	0·35 mm. mercury
Power consumption	600 watts

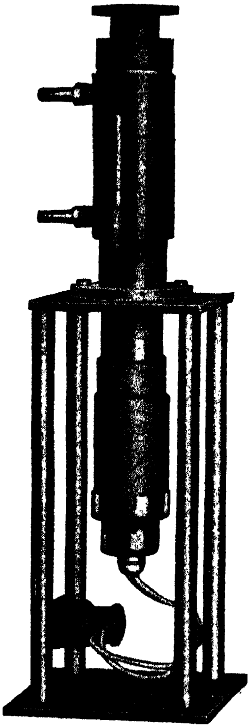

FIG. 6 (XVII^{3})
Type 02 ‘ Metrovac ’ oil-condensation pump

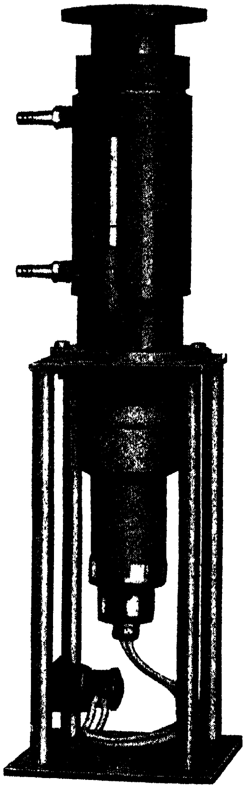

FIG. 7 (XVII^{3})
Type 03B ‘ Metrovac ’ oil-condensation pump

Type 083B ‘ Metrovac ’ Oil-Condensation Pump

The 083B pump has been developed for use where a higher pumping speed is required than that produced by the ‘ Metrovac ’ type 03B pump. Fabricated mild steel is used to construct the body of the pump, the three stage, triple jet system being of aluminium. The cooling water circulates through copper tubing which is attached around the outside of the pump body and outlet pipe.

Specification :

Type of oil	Apiezon ' B '
Volume of oil	1,350 ml.
Limiting pressure	Less than 10^{-6} mm. mercury
Pumping speed	Not less than 500 litres/sec. between 10^{-4} mm. and 10^{-5} mm. mercury
Maximum backing pressure	0·12 mm. mercury at 10^{-3} mm. mercury fore-pressure.
Power consumption	1,900 watts

' Metrovac ' Pumping Plants

Vacuum pumping plants have been developed to meet varying requirements, each plant consisting of one or more oil condensation pumps, backed by a mechanical rotary pump, the combination of pumps depending on the pumping speed and limiting pressure for which the equipment is designed.

Examples of typical pumping plants are given in Table A.

TABLE A

' METROVAC ' VACUUM PUMPING PLANTS

Pumping plant ref. no.	Type of rotary pump	Type of condensation pump	Pumping speed. litres/sec.	Limiting pressure in mm. mercury
OCP1	SR2	02	6*	10^{-5}
OCP2	DR1	02	6*	10^{-5}
OCP6	DR1	03B	30†	10^{-7}

* At pressures below 10^{-2} mm. Hg.
† „ „ „ 10^{-3} mm. Hg.

Several features are common to each pumping plant :

1. The entire apparatus comprising each plant is mounted on a baseplate to form a complete unit.
2. The inlet and outlet cooling water unions are accessibly placed and can be supplied suitable either for metal pipe or for rubber tube connexion.
3. Connexion of the electrical supply to the plant is by means of plug and socket, individual supplies going from thence to the pumps through the requisite switches and fuses.
4. A vacuum system, consisting of a vacuum tap, vapour trap fitted with a vacuum indicator and an air valve, and an oil receiver, connects the oil-condensation pump to its backing pump.

Other types of Oil-Condensation Pumps

A wide range of both glass and metal condensation pumps designed for use with organic low-vapour-pressure liquids is marketed by Distillation Products Inc.[1] This firm's types of all-glass pumps include, in addition to a single-stage model, also two-stage and three-stage fractionating pumps.

The Type GF 20A, two-stage fractionating pump (Fig. 8 (XVII[3])) is designed for air cooling and incorporates three boilers. After the unit has run for a short time, the extremely low-vapour-pressure components

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[1] Distillation Products Inc., Rochester, N.Y., U.S.A.

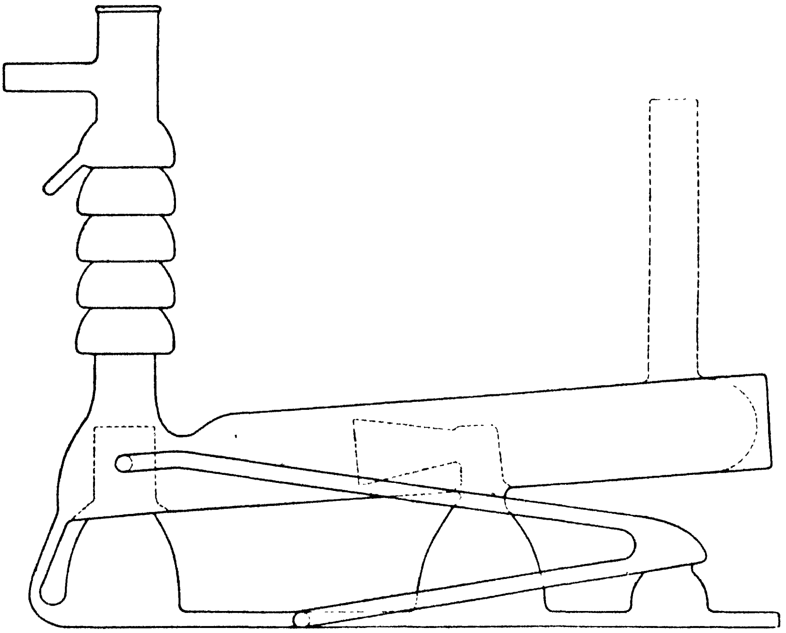

FIG. 8 (XVII^{3})

Glass two-stage fractionating pump (by Distillation Products Inc.)

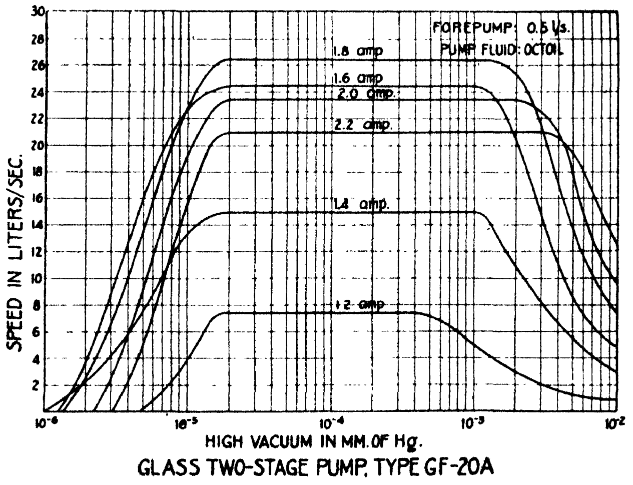

FIG. 9 (XVII^{3})

Speed *v.* high-vacuum for different heater currents (Distillation Products Inc.)

of the oil become segrated in the boiler that feeds the jet at the high-vacuum end; the constituents of slightly higher vapour pressure, which are usually water-clear, collect in the boiler for the jet at the fore-pressure end; the extreme volatiles become segregated in the catchment lobes of the vertical tube ; and the small boiler at the high-vacuum end of the pump serves as a still in which the dark-coloured, non-volatile residue collects, while the more active components are distilled and returned to the other two boilers. A variable external resistance of about 50 ohms may be used to regulate the heater input which should be maintained at from 1·3 to 2·2 amperes. The pump has a speed of from 8 to 26 litres/sec., depending on the heater input, as shown by the graph, Fig. 9 (XVII[3]). To obtain vacua of less than 10^{-6} mm. mercury, the fore-pressure must be less than 0·03 mm. mercury.

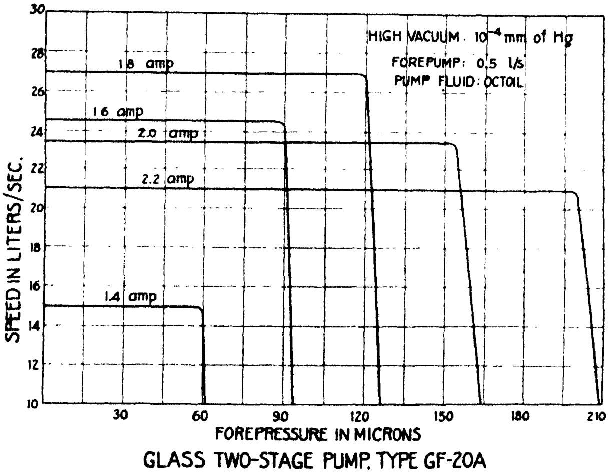

FIG. 10 (XVII[3])

Speed *v.* fore-pressure for different heater currents. (Distillation Products Inc.)

The variation of the fore-pressure with speed and heater wattage when backed by a pump having a speed of 0·5 litres/sec. is shown in Fig. 10 (XVII[3]).

Specification :

Height	14 in.
Length	16 in.
Width	5 in.
Construction	Pyrex glass
Amount of oil	125 grams
Recommended oil	Octoil
Fore-pressure	0·10 mm.
Heater power	90–260 watts
Speed	20 litres/sec. at 10^{-4} mm.
Ultimate vacuum	7 × 10^{-7} mm. at 25° C.

The type GM-220 glass-metal pump is illustrated in Fig. 11 (XVII[3]) and is designed to operate at high speeds. The variation in speed at different pressures for different heater currents is shown in Fig. 12 (XVII[3]). The effect of increasing the speed of the fore-pump to 12 litres/sec. is shown by the dotted lines in the graph extending to the right.

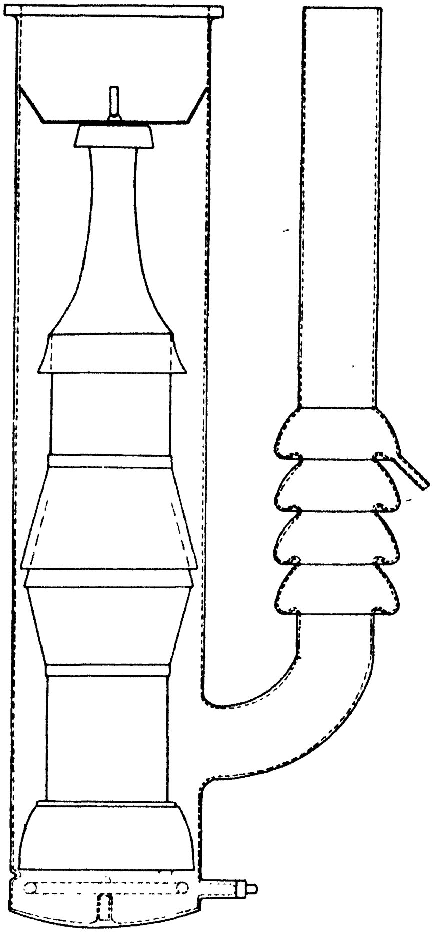

FIG. 11 (XVII[3])
Glass-metal oil-condensation pump (by Distillation Products Inc.)

Specification :

Height	20¼ in.
Amount of oil	200 grams
Recommended oils	Amoil-S ; Octoil
Fore-pressure	0·15 mm.
Heater power	130–325 watts
Speed	220 litres/sec. at 10^{-4} mm.
Ultimate vacuum	10^{-5} mm. at 25° C.

General Remarks concerning Condensation Pumps

(i) *Comparison of Types.* Condensation pumps designed for use with mercury are in general unsuitable for use with oil as the operating liquid.

There are three main features in the design of a condensation pump which may render it unsuitable for oil: (1) the gap between the jet cowl and the condensing surface may be too small, causing the gap to be bridged by an oil film ; (2) the cross-sectional areas of the jet, and of the pipe supplying vapour to the jet, may be insufficient, so that it is not possible to get an adequate supply of vapour to and through the jet without overheating the oil ; (3) the jet cowl and the vapour supply pipe to the jet may run too cool, thus causing excessive condensation of the vapour.

Consideration of the points mentioned above indicates that oil-condensation pumps should be designed so that : (*a*) there is not less than $\frac{1}{16}$ in. gap between the jet cowl and the condensing tube ; (*b*) the cross-sectional areas of the jet and of the vapour supply pipe are of generous dimensions ; (*c*) the thermal losses from the jet cowl and the vapour supply pipe are reduced to a minimum, the operating temperature of these parts approaching as nearly as possible to that of the vapour.

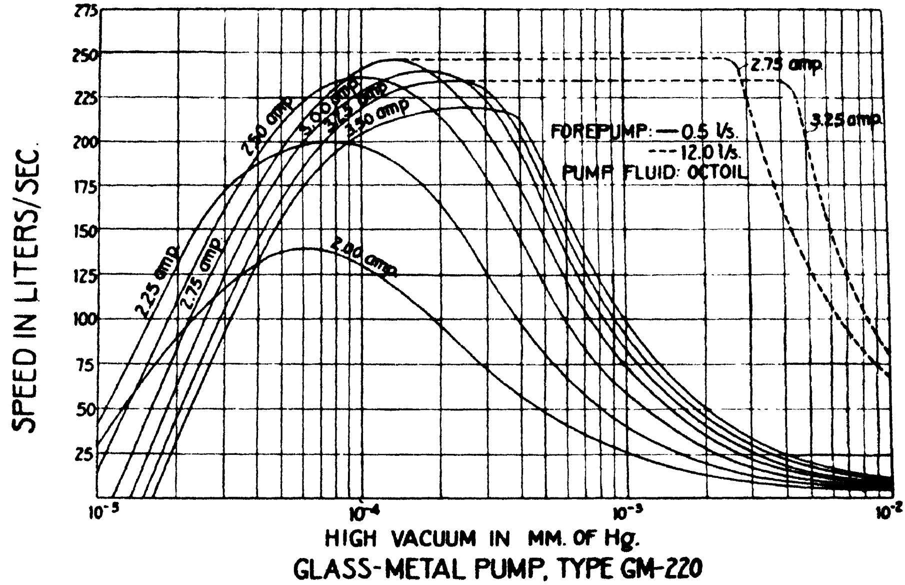

FIG. 12 (XVII^3)

Speed *v.* high vacuum for different heater currents. (Distillation Products Inc.)

(ii) *Working Conditions.* It should always be remembered that a mercury pump without a cold trap will never achieve a better vacuum than 10^{-3} mm. mercury, i.e. the vapour pressure of mercury at room temperature. This point is not always made clear when presenting figures of performance of mercury pumps. One frequently sees speeds of pumping given in conjunction with ultimate vacua of the order of 10^{-6} mm. of mercury, but the stated speed may be that attained without a cold trap, whereas the pressure of 10^{-6} mm. can be reached only by the interposition of a suitable refrigerant. ‘ Catalogue ’ speeds of condensation pumps always refer to the speed when handling ‘ permanent ’ gases, such as air or nitrogen, air being usually adopted as the standard. In such circumstances the addition of a cold trap between the pump and the vessel under evacuation will reduce the effective speed of pumping at the vessel owing to the restrictive effect of the trap on the gas flow. Where, however, condensable vapours are being handled, the cold trap serves to condense the vapours before they reach the pump, therefore the pump has to deal with only the permanent gases, so that the combination 'trap + pump' may, if suitably designed and if the proportion of condensable vapours present is sufficient, show an increase in overall speed for 'gases + vapours' compared with a similar system without the cold trap.

Another point to remember is that the 'catalogue' speed may hold good only over a relatively narrow range of pressures on the high-vacuum side, and this range may lie outside the one over which the user intends to operate the pump. Again, it must not be assumed that the stated speed can be reached when the backing pressure of the condensation pump is approaching its maximum value. It is advisable, therefore, that the user should check up that the values of ultimate pressure, pumping speed, and backing pressure, are all attainable simultaneously under his particular working conditions. This last recommendation applies equally to oil-condensation pumps.

The oil-condensation type of pump possesses the advantage that pressures as low as 10^{-6} mm. of mercury can be achieved without the use of a cold trap, thus enabling the full available speed of the pump to be utilized without restriction.

(iii) *Baffling Oil-Condensation Pumps.* Another point which requires consideration concerns the use of baffles to prevent the oil molecules 'back-streaming' from the mouth of the pump, in the opposite direction to the general flow of the gas, and into the vessel undergoing evacuation. Some oil-condensation pumps incorporate within themselves a baffle system sufficient to reduce the 'back-streaming' to a negligible value, thus enabling such pumps to be connected directly to the vacuum vessel, which may be, for example, a continuously evacuated thermionic valve or X-ray tube.

The degree of baffling necessary varies to some extent with the purpose for which the pump is intended. High-vacuum (or molecular) distillation processes which are carried out at pressures round about 10^{-3} mm. do not require a high degree of baffling, since, apart from other considerations, the effect of 'back-streaming' is not so deleterious as would be the case if thermionic devices, such as valves or X-ray tubes, were being evacuated. In general, an efficient baffling system tends to reduce the effective speed of a condensation pump. Therefore, when comparing relative speeds of oil-condensation pumps the relative efficiency of their baffling arrangements should also be taken into consideration. A simple test for determining roughly the degree of 'back-streaming' can be carried out by sealing a flat glass disk on to a flat flange directly over the mouth of the pump. If the pump baffling system is adequate, and the heater wattage is suitable, no trace of misting on the glass disk due to condensation of oil vapour can be observed even after several days' running. A pump having little or no baffling will cause a visible deposit of oil to form on the glass plate after running for less than half an hour.

Instead of being incorporated in the pump, the baffle arrangement may take the form of a separate unit installed in the pipeline between the pump and the vessel under evacuation.

Morse [1] has discussed various methods available for the construction of baffles, and has dealt with the following: (1) charcoal traps, (2) cold traps, (3) hot baffles, (4) electrical baffles, (5) mechanical baffles.

Charcoal traps have been installed in a high-vacuum pumping system described by Becker and Jaycox [2] which enabled a pressure of 2×10^{-8} mm. mercury to be attained. Anderson [3] has described a charcoal trap in which the charcoal can be outgassed by direct passage of the heating current through the granular charcoal. Any charcoal trap must, however, if it is to serve its purpose as a baffle, appreciably reduce the effective pumping speed of the system. Another disadvantage of the charcoal trap has been mentioned by DuMond and Youtz [4] who have experienced difficulty from greasy contamination when the charcoal is outgassed.

Hot baffles and electrical baffles involve relatively complicated additional equipment, and while being interesting from an academic standpoint, are probably better avoided in practice if simpler methods can be found.

A mechanical baffle possesses the advantage that no external apparatus is required to operate it; also, if properly designed, it need not cause a serious loss of pumping speed. An efficient type of conical baffle has been illustrated and described by Morse.[5]

(iv) *Precautions in Use.* When using oil-condensation pumps certain precautions must be observed. It is important to prevent the oil from becoming overheated. This condition can arise from too high a heat input, insufficient cooling water, or from allowing the backing pressure to become too high.

It is preferable to heat oil-condensation pumps electrically, as the maximum heat input is then fixed automatically by the wattage rating of the heater. Particulars of a suitable heater wattage and backing pressure to meet a given set of conditions within the capacity of the pump can be obtained from the manufacturers.

In general, it is desirable that the heaters of the pumps are not energized when the backing pressure of the pumps is higher than 0·4 mm. to 0·5 mm., and it follows, therefore, that oil-condensation pumps should never be opened up to atmospheric pressure when the oil is hot. Provided that the pump is of suitable design, rises of pressure over short intervals of time are not detrimental. If, for example, the backing pipe of the pump under operating conditions attains a temperature of 100° C. or so, any products of decomposition will be the more readily removed in the form of gas or vapour. The volume of oil in the liquid form lost from the pump in these circumstances is negligible. An increase in backing pressure beyond the safe limit will cause evaporation of the oil vapour in the pump to be reduced to such an extent that there is insufficient condensate returning to the pump boiler to maintain a stable heat cycle, with a resultant increase in the temperature of the oil.

[1] *Rev. Sci. Inst.*, 1940, *11*, 277.

[2] *Ibid.*, 1931, *2*, 773.

[3] *Ibid.*, 1937, *8*, 493.

[4] *Ibid.*, 1937, *8*, 298.

[5] Morse, Richard S., *loc. cit.*

Where oil-condensation pumps are used it is essential that no mercury should be present in any part of the system. An oil-condensation pump contaminated with a trace of mercury may eventually clear itself, but until the whole of the trace of mercury has been eliminated the pump will not produce a pressure lower than about 0·001 mm. of mercury. Even though the mercury be present only in the backing system, there is a danger that it may migrate into the condensation pump when the latter is cold.

SECTION 2: VACUUM SYSTEMS

In the previous section, the working of particular types of pumps in general use have been reviewed. Various points in connexion with the manipulation of the vacuum systems as investigated by Burrows will now be considered.[1]

Vacuum Pipelines

Formulae relating to the rate of flow of gases through pipes of different diameters may be obtained from the various text-books previously mentioned in this article. Occasionally some confusion arises regarding the units used and their nomenclature. The table given below may be of assistance when correlating pressure measurements:

Unit	Dyne/sq. cm. (or barye)	Bar	Microbar	mm. Mercury	Micron (μ)	Atmosphere
Dyne/sq.cm. (or barye)	1	10^{-6}	1	$0{\cdot}750 \times 10^{-3}$	0·750	$0{\cdot}99 \times 10^{-6}$
Bar . . .	10^6	1	10^6	750	750×10^3	0·99
Microbar .	1	10^{-6}	1	$0{\cdot}750 \times 10^{-3}$	0·750	$0{\cdot}99 \times 10^{-6}$
mm. mercury	$1{\cdot}33 \times 10^3$	$1{\cdot}33 \times 10^{-3}$	$1{\cdot}33 \times 10^3$	1	10^3	$1{\cdot}31 \times 10^{-3}$
Micron (μ) .	1·33	$1{\cdot}33 \times 10^{-6}$	1·33	10^{-3}	1	$1{\cdot}31 \times 10^{-6}$
Atmosphere	$1{\cdot}01 \times 10^6$	1·01	$1{\cdot}01 \times 10^6$	760	760×10^3	1

Some text-books refer to the unit ‘ dyne per sq. cm.’ as a barye, but the latter term is rarely used in practical high-vacuum technique, pressures being usually expressed in mm. of mercury or in microns (μ). Pumping speeds are usually expressed in litres per second.

When the mean free path of the gas molecules becomes comparable with the diameter of the tube, the frequency of the collisions between the molecules themselves becomes small compared with collisions between the molecules and the walls of the tube. Under such conditions Poiseuille's Law no longer holds, and the pumping speed of a pipe, for a given gas, becomes independent of the pressure as has been shown by Knudsen. The following approximations have been derived from the text-book formulae, and may be found useful when considering pipe sizes.

If P = pressure in microns (μ), and D = diameter of pipe in cm., then up to values of $P \times D = 10$, the pumping speed of a pipe for air in litres per second is roughly $10D^3/L$, where L is the length of the straight pipe in cm. For example, at pressures from zero up to 5 μ, a pipe 2 cm. diameter and 16 cm. long has a pumping speed of about 5 litres per sec. for air.

The pumping speed of an aperture of area A sq. cm. whose greatest width is less than the mean free path of the molecules at the pressure obtaining, is roughly $10A$ litres per sec.

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[1] Burrows, *J. Sci. Inst.*, 1943, *20*, 21.

If S is the combined speed of a system consisting of a condensation pump exhausting through a pipe or pipes, and if S_1 is the speed of the pump, and S_2, S_3, &c., be the individual speeds of the pipes in series with the condensation pump and with each other, then $\frac{1}{S} = \frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}$, &c. That is to say, if the reciprocal of a speed is regarded as a resistance, the overall resistance of a pumping system is the sum of the resistances of the separate parts in series. This point is of importance when arranging the length and diameter of pipe connexions on the high-vacuum side of condensation pumps. For example, if a pump having a speed of 20 litres per sec. is connected to a pipe having a speed of 5 litres per sec. at the operating pressure, then the overall speed of the combination is only 4 litres per sec. Thus a high-speed condensation pump offers no advantage unless the pipe connexion between the pump and the vessel possesses a correspondingly high pumping speed. It follows that the pipe connexions on the high-vacuum side of condensation pumps should always be as large in diameter and as short as possible. If it is necessary for constructional reasons to have long pipe connexions, then these should be confined to the backing side, since in that position they operate at higher pressures and therefore, for a given size, offer less resistance for a given gas flow.

When considering the relative pumping capacities of the various units in a pumping system it is often convenient to refer to the gas throughput in terms of litres-μ per sec., that is, the product of the speed in litres per second and the corresponding pressure in microns (μ). The value of the gas throughput in litres-μ per second will remain constant throughout the system assuming that the temperature is uniform and that there are no leaks.

If the speed of the primary condensation pump in litres per second is known together with the corresponding pressure in μ on the high-vacuum side, then the value in litres-μ per second for the system is determined. This information enables the various pumping units in the system to be suitably proportioned.

Suppose, for example, that a condensation pump has a speed of 20 litres per sec. when operating at a pressure of 1μ on the fine side, and that under these conditions the maximum permissible backing pressure of the pump is 100μ (0·1 mm.). Then the least permissible speed of the backing pump at 100μ is given by $(20 \times 1)/100 = 0{\cdot}2$ litre per sec. $=$ 200 ml. per sec. (This is the speed according to Gaede's definition and must not be confused with the displacement of a mechanical pump.) If the condensation pump operated at a pressure of $0{\cdot}1\ \mu$ ($= 10^{-4}$ mm.) on the fine side under otherwise similar conditions, then the least permissible speed of the backing pump would be $(20 \times 0{\cdot}1)/100 = 0{\cdot}02$ litre per sec. $=$ 20 ml. per sec. It is apparent that for a given speed on the fine side of the condensation pump, the required pumping capacity of the backing pump varies in proportion to the fine side pressure; the higher the fine side pressure, the larger must be the backing pump.

Again, for a given rate of flow of gas, the pumping speed of the backing pump determines the backing pressure against which the condensation pump operates.

Detachable Joints and Jointing Media

It is essential in a high-vacuum system that all materials in that system should have a vapour pressure less than the lowest pressure desired in the system. Hence the jointing materials and sealing media used for the joints of high-vacuum equipment must possess very low vapour pressures.

Burch and Sykes[1] have pointed out that a pump having a speed of 20 litres per sec. for air can reach a pressure only three times lower than the saturation pressure of the jointing material, assuming that 1 sq. cm. of jointing material is exposed to the vacuum.

The main requirements which a detachable joint should possess can be summarized as follows: (*a*) freedom from doubt as to its vacuum tightness; (*b*) minimum penetration of sealing medium into the vacuum space; (*c*) ease of dismounting and reassembly; (*d*) simplicity of fabrication. A useful form of detachable joint consists of two flat flanges, one flange being a little larger in diameter than the other, as shown in Fig. 13 (XVII[3]). Where a specially high degree of vacuum is required, as in continuously evacuated radio valves, great care must be taken to ensure the flatness of the surfaces in contact, the flanges, if of metal, being accurately machined, this process being supplemented if necessary by a final grinding operation. Glass and porcelain flanges are ground flat, the technique of this operation being similar to that adopted for grinding optical surfaces,[2] using a rotating lap and suitably graded abrasive. The degree of flatness of the flange can be tested by means of a glass disk having a known degree of flatness, the shape and number of interference 'rings' produced when the disk is brought into contact with the flange indicating the contour of the flange, due allowance being made for any out of truth of the disk.[3]

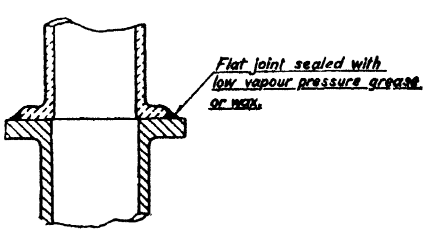

FIG. 13 (XVII[3])
Detachable joint

Flat joints which have frequently to be dismantled, as in laboratory apparatus, are best sealed by a low-vapour-pressure grease such as Apiezon L grease for use on the high-vacuum side of condensation pumps, and Apiezon M grease on the backing side. With joints of a more permanent nature, as on industrial apparatus, one of the Apiezon waxes should be used for sealing instead of grease, Apiezon W 40 or Apiezon W 100 for joints at room temperature, or Apiezon W for joints which become warm under operating conditions.

The surfaces to which any of the waxes are to be applied should always be raised in temperature up to the melting-point of the particular grade of wax employed before attempting to seal the joint. The aim should be to make a smooth, neat, uniform fillet of wax free from lumps, excrescences, and pin-holes. The achievement of these objects will be assisted if a small pointed bunsen flame is finally run round the joint to smooth out any irregularities in the wax. Care should be taken to keep the flame on the move in order to avoid burning the wax.

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[1] *J. Inst. Elect. Eng.*, 1935, *77*, 130.

[2] Strong, *Modern Physical Laboratory Practice*, pp. 39–51 (London: Blackie & Son, Ltd.).

[3] *Ibid.*, 63–66.

A material suitable for sealing unground joints, as in testing operations where it is necessary temporarily to blank off a portion of the apparatus, is known as Apiezon Sealing Compound Q. This material is firm at room temperature, but sufficiently soft to allow of easy moulding by hand. It is usually applied by rolling out a portion of the material between the palms of the hands into the form of a long, thin ' sausage ', placing this round the joint, pressing firmly into position with the fingers, and then smoothing round until a neat fillet is obtained. Although Apiezon Sealing Compound Q is primarily intended for use on the backing side of condensation pumps, it has been used successfully on the high-vacuum side, but it is not recommended for use in regions which require an extremely high degree of evacuation to be maintained, as in thermionic valve work. In such cases Apiezon L grease or one of the Apiezon waxes would be more suitable.

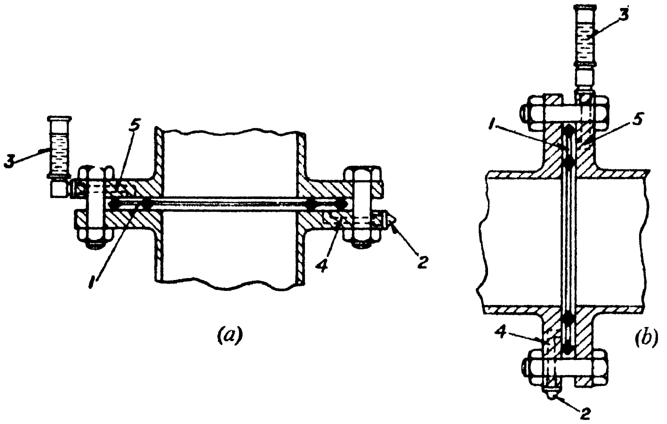

FIG. 14 (XVII[3])

Oil-sealed joint (*a*) for vertical pipes, (*b*) for horizontal pipes [1]

The faces of flat vacuum joints should be put together clean and dry, the rough vacuum, such as that provided by the rotary backing pump, being then applied so as to pull the faces together, the vacuum so obtained giving an indication as to whether the faces are in proper contact. If the conditions appear to be satisfactory, then the sealing medium should be applied as a final operation round the outside of the joint.

Descriptions of various ingenious methods of making vacuum-tight joints appear from time to time in British and American technical journals. For example, an article [2] dealing with the design of the Minnesota Electrostatic Generator, mentions that the vacuum joints between the porcelain bushings are sealed with a mixture of eleven parts of Apiezon Wax W and one part of Apiezon J oil, the hot wax being squirted into the annular space from modified grease guns.

[1] Based on British Patent No. 451,417.

[2] Williams, Rumbaugh, and Tate, *Rev. Sci. Inst.*, 1942, *13*, 204.

A form of oil-sealed joint, suitable for the flanges of metal pipes of about $1\frac{1}{2}$ in. bore or larger, and which can be arranged for either (*a*) vertical pipes, or (*b*) horizontal pipes, is shown in Fig. 14 (XVII^3). The soft copper ring 1 is formed with ridges and also with holes to enable the sealing oil to pass from one side of the ring to the other. Low-vapour-pressure sealing oil is introduced through the nipple 2 and flows through the hole 4 in the flange, thence around and over the joint ring 1, finally passing out through the hole 5 into the sight glass 3. So long as oil is visible in the sight glass 3, no question as to the vacuum tightness of the joint between the flanges need arise.

Another useful type of oil-sealed joint for vertical metal pipes is shown in Fig. 15 (XVII^3). The inner and outer coned portions 1 and 2 respectively are locked together by means of the threaded ring 3 which is provided with slots in which the prongs of a suitably shaped key engage. The annular channel above ring 3 is flooded with low-vapour pressure oil which acts as a vacuum seal.

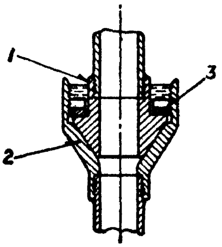

FIG. 15 (XVII^3)
Conical oil-sealed joint

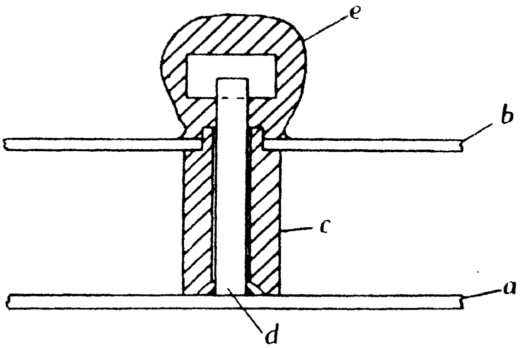

FIG. 16 (XVII^3)
Joint between insulated electrodes

Insulating Joints. Rigid joints between insulated nickel flanges for a vacuum tube, which were to run at bright red heat, can be secured by using a ceramic setting compound as sold for the coating and setting of heater wires for electric furnaces.[1] The method can be understood from Fig. 16 (XVII^3). The wire *d* is butt-welded to the one plate *a*, and a suitably formed ceramic insulator *c* is pushed over the wire. The insulator is then locked, for instance by welding a piece of nickel strip on the end of the wire. The second plate *b*, which has a hole of the diameter of the shoulder of the insulator *c*, is then put in position and fastened by a bead of the setting compound which finds a hold on the piece of nickel strip. After drying, the parts are fired in a flame or in a vacuum or hydrogen furnace. Three symmetrically arranged joints of this type give a perfectly rigid assembly of the two flanges.

If specially made insulators are not available, insulators known as fish-spine beads can be used, and a number of variations suggest themselves according to the problem. The essential feature of Ehrenberg's method is to fix metal plates spaced by ceramic insulators in position by beads of a setting compound that are afterwards sintered.

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[1] Ehrenberg, *J. Sci. Inst.*, 1939, *16*, No. 5.

Vacuum Gauges and Indicators

Discharge Tube. A convenient form of vacuum indicator consists of a simple glow discharge tube. The type shown in Fig. 17 (XVII[3]) is suitable for metal apparatus. The terminal of the discharge tube should be connected to a source of high tension current, such as that from a trembler induction coil, providing a spark in air about $\frac{3}{8}$ in. to $\frac{1}{2}$ in. long. The following approximate relationships exist between the discharge as observed in a discharge tube of the type shown and the corresponding air pressure :

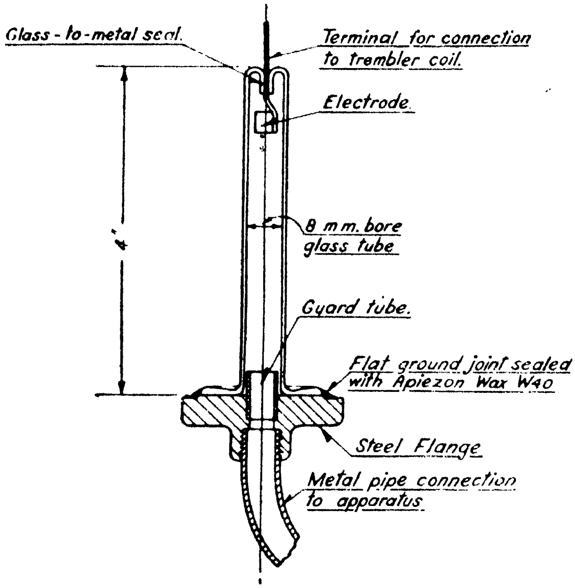
Glass-to-metal seal
Terminal for connection to trembler coil.
Electrode.
8 mm. bore glass tube
Guard tube.
Flat ground joint sealed with Apiezon Wax W40
Steel Flange
Metal pipe connection to apparatus

FIG. 17 (XVII[3])
Glow discharge tube for use with metal apparatus

$\frac{1}{2}$ cm. diameter column of glow discharge . . . . = 10 mm. of mercury
First visible striations . . . . = $1\frac{1}{2}$ mm. of mercury
Striations pitched 1 cm. apart . . . . . . = $\frac{1}{2}$ mm. of mercury
Green fluorescence on inside walls of discharge tube. . = 0·01 mm. of mercury
Black-out in dark (under vacuum conditions) . . . = 0·001 mm. of mercury (or less)

The discharge tube also enables an estimation to be made of the kind of gas or vapour present, thus :

Appearance	Kind of gas
Red or pink	Air
Greenish grey	Decomposed oil
Faint (transparent) blue	Water vapour

The McLeod gauge suffers from several serious disadvantages as a practical instrument for routine work. It is an unwieldy device, and is capable of giving only ' spot ' readings—a serious drawback where a continuous indication is required as in testing for leaks. A McLeod gauge which employs mercury is not safe to use in vacuum systems incorporating oil-condensation pumps. Also the McLeod gauge measures the pressure of only the permanent gases present; easily condensable vapours are changed to liquid under the conditions of compression which occur when taking a reading.

A description has recently been published [1] of a McLeod type of gauge which uses Apiezon oil ' B ' as the operating liquid instead of mercury. Special features are incorporated to assist in the removal of the air dissolved in the oil. The reservoir is in gas communication with the bulb, and the oil is displaced by a plunger externally controlled. The bulb has a volume of 300 ml., and the capillaries have a bore diameter of 1·44 mm. There is no evidence of sticking in the capillaries. For single measurements at pressures of 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6} mm. of mercury the gauge is considered accurate to about 1, 2, 8, and 25 per cent, respectively. The equivalent compression ratio for the gauge is $3{\cdot}5 \times 10^{-7}$. To degas the oil it is necessary to raise it about five times, for half-hour periods, to the freely vaporizing state while the diffusion pumps are in operation. The whole instrument is kept continuously at a low pressure (10^{-2} mm. of mercury or less), thus enabling it to be used, at intervals of several months, without further heat treatment, for the measurement of pressure within its range. Various advantages are claimed on account of the adoption of Apiezon oil instead of mercury, including the use of large bore capillary tubing for the construction of the gauge, and the fact that the gauge may be connected directly to systems incorporating oil-diffusion pumps without the special precautions which would be necessary if mercury were used.

The Pirani gauge is, in general, a convenient form of high-vacuum gauge for the pressure region 10^{-2} mm. to 10^{-4} mm. of mercury. It must be remembered, however, that the sensitivity of this type of gauge is proportional to the specific heat and inversely proportional to the square root of the molecular weight of the vapour in the gauge. Therefore, since the gauge is usually calibrated with air or nitrogen, it will not give correct readings of the total absolute pressure if organic vapours are present. Another peculiarity of this gauge is that the filament tends to become ' poisoned ' by organic vapours, with the result that over a period of time the readings finally obtained bear no relation to the original calibration on air. Periodical recalibration is, therefore, desirable.

Within its somewhat limited pressure range, the Pirani gauge finds its most useful application where it is desired to have a convenient means of obtaining dial readings of pressure fluctuations, but where accurate absolute pressure readings are not required.

A low vapour-pressure oil manometer, arranged as shown in Fig. 18 (XVII[3]) can be used for determining total absolute air and vapour pressures above about 0·1 mm. of mercury. The sensitivity of such an oil manometer will be about fifteen times greater than a mercury manometer owing to the fact that the density of the oil is about 1/15th that of mercury. The branch A is connected to the apparatus in which it is desired to measure the degree of vacuum, and branch B is continuously evacuated by means of a small-capacity oil-condensation pump backed by a rotary pump. The loop D contains a low-vapour-pressure liquid such as an Apiezon oil. The level at *b* can be regarded as representing zero pressure, and the difference between the levels *a* and *b* indicates the absolute pressure at *a*. With oil, a difference between the levels *a* and *b* of, say, 15 mm. indicates a pressure of about 1 mm. of mercury in the connexion A leading to the apparatus. Before using the gauge, the manometer tube should be gently warmed with a gas flame while under evacuation in order to accelerate the removal of dissolved air. A cock C should be provided as shown in order to equalize the pressure in the limbs when the apparatus is opened up to atmosphere.

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[1] Bannon, *Rev. Sci. Inst.*, 1943, *14*, 6.

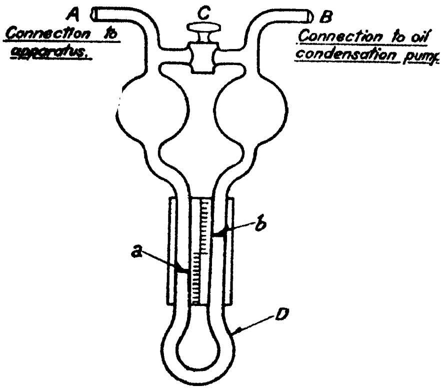

FIG. 18 (XVII^3)
Low-vapour-pressure oil manometer

The ionization gauge is a popular form of gauge for measurements of pressure within the range from 10^{-3} mm. to 10^{-7} mm. of mercury. Admittedly it is not an absolute gauge, but it is fairly simple to calibrate, and is not as delicate to manipulate as the Knudsen gauge, although the latter possesses the advantage that it is a true absolute gauge.

Since the ionization gauge employs a heated filament, it suffers to some extent from the same disadvantages on this account as the Pirani gauge does when organic vapours are present.

For this reason it is usually desirable to interpose a cold trap containing, for example, a mixture of carbon dioxide ‘ snow ’ and acetone, between the ionization gauge and the pump, if there is a possibility that excessive quantities of oil vapour may reach the gauge, such as might occur with an oil-condensation pump which is inadequately baffled. A cold trap may be employed where the gauge is used for determining pumping speeds, as the speed usually required is that of the permanent gas passing through the system. When the gauge is used, however, for measuring the ultimate vacuum, or lowest pressure attainable, such as that achieved by an oil-condensation pump, the cold trap must be omitted, since it is the vapour pressure of the liquid used in the pump which determines the reading required and the vapour would be condensed before it reached the gauge if a cold trap were used. When determining ultimate vacua by means of an ionization gauge, the oil-condensation pump should incorporate an efficient baffling arrangement, so as to reduce back-streaming of oil molecules to a minimum.

It should be noted also that the sensitivity of an ionization gauge depends on its physical dimensions and the lay-out of its electrodes together with the particular arrangement of the electrical circuit adopted.

In addition to the information given in the text-books previously mentioned, several articles containing useful details of the design, construction, and use of various forms of ionization gauge have been published.[1]

The ' Metrovac ' Ionization Gauge [2] has been developed to meet the need for an industrial form of demountable ionization gauge which can be left in the charge of comparatively unskilled operators. In order to eliminate the need for outgassing, the electrodes of the gauge, instead of being enclosed in a glass envelope, are placed directly inside the vessel where the pressure is to be measured.[3] The gauge and its control unit together form a measuring system which ensures completely automatic operation without the need for outgassing.

The Knudsen gauge, although not generally accepted as a practical instrument for routine work, possesses the outstanding advantage that, if suitably designed, it indicates very closely the absolute pressures of both gases and condensable vapours irrespective of their nature or condensability, which cannot be said of the McLeod, Pirani or ionization gauges.

Knudsen gauges can be constructed to cover a pressure range similar to that of the ionization gauge, namely, 10^{-3} mm. to about 10^{-7} mm. of mercury. An interesting and informative article has been published by DuMond and Pickles describing a practical form of this type of gauge.[4] Incidentally the article gives an excellent summary of the various arguments for and against the use of the McLeod, Pirani, ionization, and Knudsen gauges. Other recently developed gauges of this type are described by Hughes [5] and by Lockenvitz.[6]

Avoidance and Detection of Leaks

The question of leaks is an ever-present problem when considering the design and operation of high-vacuum apparatus. It is always worth while taking special care when designing and constructing the apparatus to ensure that the possibility of leaks occurring under operating conditions is reduced to a minimum, and that the places where leaks might occur are left accessible and, so far as possible, capable of being easily made good should a leak develop. If proper precautions are not taken initially, it will probably be found that the operator spends his time in searching for, and—we hope—in eliminating leaks, instead of being more usefully employed in looking after the apparatus under evacuation.

The component parts of complicated equipment should be tested individually for leaks before the complete apparatus is assembled.

Leaks in glass apparatus may be located with the aid of a spark coil, provided that the pressure in the system can be pumped down to the point at which a discharge can pass through the remaining gas. The spark coil should have a spark gap in parallel with its secondary so as to prevent unduly high potentials being reached which might cause sparking through weak spots in the glass. One terminal of the secondary of the coil should be connected to an electrode sealed in the system. A wire from the other terminal is then moved over all parts of the system, being held by means of a rod of insulating material. When the exploring wire is near a leak, it will be found that the discharge lights up, and glows brightly in the immediate vicinity of the leak.

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[1] Jaycox, and Weinhart, *Rev. Sci. Inst*, 1931, *2*, 401 ; Montgomery, *ibid.*, 1938, *9*, 58 ; Morse and Bowie, *ibid.*, 1940, *11*, 91 ; Bowie, *ibid.*, 1940, *11*, 265 ; Rainwater, *ibid.*, 1942, *13*, 118.

[2] Metropolitan-Vickers Electrical Co. Ltd.

[3] Blears, J., *Proc. Roy. Soc.*, *A*, 1946, *188*, 62.

[4] DuMond and Pickles, *Rev. Sci. Inst.*, 1935, *6*, 362.

[5] Hughes, *ibid.*, 1937, *8*, 409.

[6] Lockenvitz, *ibid.*, 1938, *9*, 417.

Alternatively, a discharge can be passed continuously through the residual gas in the system, the places where leaks are suspected being sponged or brushed over with a highly volatile liquid such as alcohol or ether. Assuming that the residual gas consists of air, then the colour of the discharge will change from pink to watery blue when the ether vapour passes through the hole causing the leak. If the apparatus is of metal, a glass discharge tube of the type shown in Fig. 17 (XVII[3]) can be used as an indicator. Alternatively, an ionization gauge on the high-vacuum side, or a Pirani gauge on the backing side of the condensation pump, can be used as indicators of the change in the conditions brought about by the leakage into the system of the ether vapour used for testing, since the introduction of the organic vapour will cause an alteration in the rate of emission of the gauges.[1, 2]

Grease-sealed joints sometimes give trouble, as the grease may ' track ', owing, for example, to occluded air bubbles. A path once formed can give a lot of trouble either as a continuous or intermittent leak, and the writer's experience is that the leak-hunter will generally find that it is the last and probably most inaccessible joint to be tried which has been responsible for his difficulties !

Grease-sealed joints which are thought to be leaking are usually tested by running a finger round the joint over the grease and at the same time carefully watching the vacuum indicator to see whether the pressure alters.

Correctly designed metal joints sealed with oil, as described previously, possess the great advantage that if the oil can be seen it can be made to act as an indicator ensuring that the joint is quite vacuum-tight.

The location and detection of leaks in metal apparatus can be effected by means of a compressed air test in conjunction with a ' shut-down ' vacuum test. The shut-down vacuum test shows whether a leak is present or not, the location of the leak being determined by the compressed-air test.

In order to localize possible sources of leaks in metal high-vacuum apparatus the use of castings should be avoided, since they frequently contain porous areas consisting of a large number of minute leakage paths.

Where steel is employed, a welded construction should be adopted, using best-quality rolled plate and solid drawn tube. Leaks are then almost always situated in the welds.

Copper pipe joints should be either silver soldered or screwed and soft soldered, the threads being first thoroughly ' tinned ' in the latter case. When forming copper-pipe bends care should be taken to keep the metal properly annealed. If it is allowed to work-harden, there is always a danger that hair cracks or porous areas may develop on the outside of the bend where the metal is stretched. Rolled steel bar occasionally contains non-metallic inclusions lying axially along the bar. Therefore, if disks are

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[1] Rainwater, *ibid.*, 1942, *13*, 120.

[2] Cuykendall, *ibid.*, 1935, *6*, 371.

required to be vacuum-tight across their faces they should be cut from flat plate and not turned or sawn off the bar.

All welds and joints must be kept free from paint and similar coatings until after the vacuum tests have been satisfactorily completed.

Compressed-Air Test. This method of locating the actual source of leaks can be applied to metal components capable of safely withstanding the internal air-test pressure, usually something of the order of 60 lb. per sq. in. There should be no difficulty in arranging that small metal components are suitable for the compressed-air test, since, in any case, they have to be capable of withstanding the external atmospheric pressure of 15 lb. per sq. in. If the test pressure is to be maintained safely in the case of large vessels, however, the thicknesses of the plates may tend to become excessive, so that either the test pressure must be reduced, or measures adopted in the design to prevent the plates from being overstressed. One such method is to weld both sides of the joint and introduce the compressed air in between the welds as shown in Fig. 19 (XVII³).

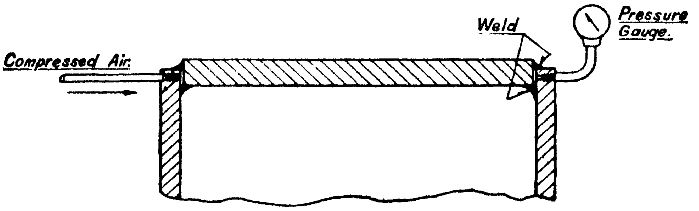

FIG. 19 (XVII³)
Compressed-air test of welded joint

After blocking up the ends of any open pipes, and arranging for a flexible tube connexion to the compressed air supply, small components can be completely immersed in a tank of water. Larger components should be manœuvred so that little walls about $\frac{3}{4}$ in. high made from Apiezon Q sealing compound can be fixed along both sides of each weld or joint where a leak might occur, care being taken to keep the welds themselves entirely free from the compound. The idea of the little walls is to form a trough, so that each weld can in turn be completely covered with a layer of water about $\frac{1}{2}$ in. deep. While under water, the weld should be examined slowly and carefully throughout its length. A stream of bubbles gives an obvious indication of a leak. Small bubbles adhering to the surface should be wiped off with a water-colour brush and their position carefully examined to see whether a further bubble tends to grow.

It is possible to form a rough estimate of the probable size and rate of formation of bubbles which one may expect to find by means of the ‘ compressed-air-under-water ’ test. The method used by the writer makes the following assumptions : (i) that the leak is due to one hole ; (ii) that this hole allows a definite quantity of air to pass through per unit time (litres-μ per sec.) in either direction in proportion to the pressure difference across the ends.

Knowing the size of the vessel and the rise of pressure in it over a given time due to a leak, we can calculate the rate of flow of air *into* the vessel due to the external atmospheric pressure.

The size of the bubbles formed during the compressed-air test combined with their rate of formation, measures the rate of flow of air *out* of the vessel due to the internal compressed-air test pressure.

Let T = time in seconds to produce a rise of pressure of P microns (μ) in a vessel of volume V litres.

t = time in seconds to form bubbles having a total volume v ml. at atmospheric pressure (760×10^3 microns).

Compressed-air test pressure = 75 lb./sq. in. abs.
Atmospheric pressure = 15 lb./sq. in. abs.

Then rate of flow of air *into* the vessel $= \dfrac{VP}{T}$ litres-μ/sec. . . (1)

Also rate of flow of air *out* of the vessel $= \dfrac{v \times 760 \times 10^3}{t}$ ml.-μ/sec.

$= \dfrac{v \times 760}{t}$ litres-μ/sec. . (2)

Thus we have the proportion

$$15 : 60 = \frac{VP}{T} : \frac{v \times 760}{t} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

from which

$$\frac{v}{t} = \frac{VP}{T \times 190}$$

As an example of the application of equation (3), suppose a 20-litre vessel has a hole which causes a rise in pressure of 0·5 mm. of air (500μ) during a 14-hour (50,000-sec.) shut-down vacuum test.

Then V = 20 litres, P = 500μ, T = 50,000 sec.

Thus

$$\frac{v}{t} = \frac{20 \times 500}{50{,}000 \times 190} = \frac{1}{950} \text{ ml./sec.} = 10^{-3} \text{ ml./sec. (approx.)}$$

$$= 1 \text{ cu. mm./sec.}$$

Let $v = 1$, then diameter of bubble = 1¼ mm. Thus on a compressed-air test at 75 lb./sq. in. abs. (60 lb./sq. in. gauge) we should expect to find a 1¼ mm. diameter bubble every second, or a 1½ mm. diameter bubble every 2 seconds and so on.

The compressed-air test calls for considerable care and patience when watching for the growth of bubbles caused by very small holes. It sometimes happens that small holes are not detected on the first compressed-air test, but are located at a second attempt, carried out more carefully, after a shut-down vacuum test has proved that there is a leak to be found. The figures and examples given will be of interest as not only indicating the order of leakage which may be detected, but also as showing methods of calculation which can be adopted by the vacuum technician when dealing with problems of this nature. Thus, for a vessel of given size undergoing a shut-down vacuum test, the rate of rise of pressure in the vessel gives a measure of the rate of leakage.

The difficulty of detecting very small holes serves to emphasize what has already been written regarding castings, that is, the importance of doing everything possible to eliminate porous areas in high-vacuum work.

In a porous area, the cross-sections of the individual passages may be so small as to evade detection by the compressed-air test, but their total number may be so large as to give rise to a troublesome leak.

Leak detectors employing the principle of the mass spectrometer have been successfully used for detecting leaks in vacuum systems.[1] The instrument is attached to the vacuum system and, as the latter is pumped, a jet of helium gas is directed over various parts of the system. This gas is drawn through the leak and passes through the mass spectrometer which separates and measures the helium molecules, by reason of their mass, from other molecules in the atmosphere. The operator can thus locate the section and the leak in a relatively short time.

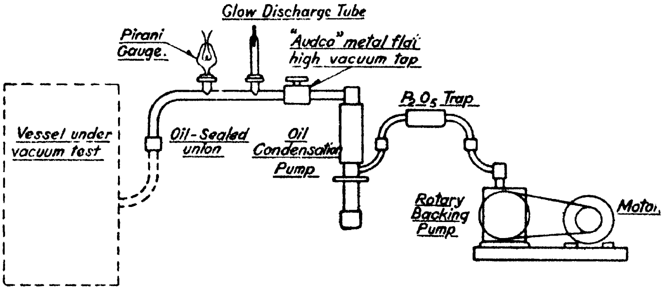

FIG. 20 (XVII³)
Equipment for 'shut-down' vacuum test

This particular method, while achieving some degree of popularity in the U.S.A., cannot be readily applied in England owing to the scarcity of helium.

Shut-down Vacuum Test. Before a shut-down vacuum test is attempted, it is important that all water and grease should be completely removed from the interior of the vessel. Scale should be removed from metal parts, and all interior surfaces made clean and smooth.

A typical set-up for vacuum testing a metal vessel is shown in Fig. 20 (XVII³). The parts shown in full lines can be assembled permanently as a standard testing unit, a metal pipe connexion being made as required between the oil-sealed union and the vessel under evacuation. No joints containing rubber should be permitted on the high-vacuum side of the oil-condensation pump. In order to assist in the liberation and removal of traces of contaminant which may have been left behind after cleaning out, the vessel should be heated, for example, by means of a ' woolly ' gas flame, during pumping. The higher the temperature the better, the limit usually being determined by the waxed or soft soldered joints on the apparatus. When the pump has got down to a vacuum black-out as shown by the discharge tube (Fig. 20 (XVII³)), the vessel should be allowed to cool down while pumping, and when at, or near, room temperature, it should be shut down under vacuum by means of the 'Audco' tap. If the reading of the Pirani gauge now indicates a progressive and uniform rise of pressure over several hours, a leak probably exists. This can be confirmed by reference to the discharge tube, which will show a pinky glow if air is present.

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[1] Thomas, Williams and Hipple, *Rev. Sci. Inst.*, 1946, *17*, 368.

If the vessel is quite vacuum-tight but has not been thoroughly cleaned out, the pressure after shutting down as denoted by the Pirani gauge may first rise, but will afterwards tend to approach a constant value, showing the presence of contaminating vapours. In such circumstances the discharge tube glow will not have the same clean pink appearance as when only air is present, but will show a watery blue or greenish-grey colour. The vessel should, therefore, be reheated with the object of driving out the remaining contaminants.

The aim should be to achieve a vacuum black-out, or a faint trace of green fluorescence, as indicated by the discharge tube, at the end of a vacuum shut-down of several hours, the actual length of time depending on the size of the vessel. As a rough guide, the writer has found that for vessels of from 10 to 20 litres capacity a shut-down vacuum test of 12 hours is usually sufficient. For larger vessels a longer shut-down test is desirable while for smaller vessels the duration of the shut-down test may be reduced.

Surface Treatment

The condition of the surfaces exposed to the vacuum becomes of increasing importance as the lower pressure regions are reached. The lower the pressure to be obtained, the greater must be the care expended on the preparation and treatment of the surfaces.

In order to minimize the quantity of gas evolved from such surfaces when very low pressures are desired, it is essential that the surfaces be (*a*) clean, (*b*) smooth, and (*c*) free from porosity.

The liberation and emission of occluded gases is assisted and accelerated by heating the parts concerned, either by radiation, or by induction where conditions are favourable. Glass parts are usually best heated *in situ* while being pumped out. Metal parts which are required for use at the very lowest pressures should undergo a preliminary 'baking out' in a vacuum furnace at as high a temperature as possible.

In other cases, however, it is usually sufficient to ensure cleanliness by washing the polished metal parts with an absolutely clean rag moistened with ether, followed by soap and water, then thoroughly rinsing in hot water, and drying in a jet of compressed air. This method will help to eliminate particles of fluff, which might otherwise be left behind after using the cleaning rags.

When using metal parts, smooth, preferably polished, surfaces are desirable since a rough surface presents a much greater effective area from which gas evolution can occur. In this connexion Strong,[1] suggests that for certain applications steel tanks used as vacuum containers should be cleaned out by sandblasting and then coated internally with a layer of Apiezon Wax W, so as to present a smooth, gas-free surface.

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[1] Strong, *Modern Physical Laboratory Practice*, pp. 126, 176 (London : Blackie & Son, Ltd.).

Use of ‘ Getters ’

A ‘ gettering ’ process may be used which, by means of a reagent, improves the vacuum after seal-off from the exhaust system. The reagent employed is usually a chemically active metal such as calcium, barium or magnesium, and is known as a ‘ getter ’. The use of getters is of special importance in connexion with the manufacture of sealed-off equipment contained in glass envelopes such as thermionic valves, cathode ray tubes, &c. The getter is evaporated or volatilized by heating electrically while in the vacuum container just before sealing off from the pumping system. During volatilization the getter combines with the residual gases in the vacuum container which are fixed as chemical compounds deposited on the walls of the envelope. Most getters also absorb the small quantities of gas which may be released after the container is sealed off.

In practice, it is usual to mount a small amount of the getter in pellet form on a small disk or cup of out-gassed nickel and heat by eddy currents. The design of the vacuum container is arranged so that the getter metal on volatilizing is directed away from the internal electrical parts on to a remote portion of the envelope, where it forms a deposit which will continue to absorb gases, and so help to maintain the degree of vacuum requisite for the efficient operation of the valve or tube during its working life.

CHAPTER XVIII [3]

MICRO-GAS ANALYSIS

SECTION 1: VOLUMETRIC METHODS

QUANTITATIVE micro-methods for gas analysis are of special importance in certain types of biological and other work where small amounts of gas only may be available. They are also of value in other types of research where numerous samples are required during an investigation to ascertain the course of a reaction, &c. In high-vacuum work the method is also of great assistance when the total quantity of gas or vapour is very minute. The ordinary macro technique is generally not suitable when dealing with relatively small amounts though in some cases it can be modified or adapted for the analysis of volumes as small as 1 or 2 ml.

Various physical methods can be employed in such forms of analysis. These include the use of the spectroscope, measurement of thermal conductivity, or dielectric constant (*see* Section 3), low-temperature condensation, followed by fractional distillation, density determination and accurate measure of small gas volumes after various treatment. Many of these methods are recorded in their approximate places throughout the text. This section will be restricted to methods which have been grouped under the general title of *volumetric methods.* This classification was made by Hartridge and will be followed, in the main, in the following description of volumetric methods.[1]

(*a*) Dry-gas Variable-Volume Method

The confining medium in this method is mercury, and solid reagents are employed. The gas is measured at all times as ‘ dry gas ’. The gas is contained in a minute glass tube calibrated in volumes. By special devices solid absorbents or adsorbents for particular gases are introduced—the original Bunsen method—and the change in volume recorded. The solid reagents are introduced at the end of a platinum wire, e.g. fused potassium hydroxide for carbon dioxide. Owing to the minute quantity of gas dealt with, the use of taps would introduce too large an error. It is therefore necessary to have a capillary tube with a siphon arrangement leading to a mercury trough. The sample is introduced from an inverted tube in the trough (*cf.* the Bone and Wheeler apparatus). By jacketing the capillary it can also be used for volatile hydrocarbons. It has also been adapted for studying the explosion of gases (with special spark-gap to prevent trapping of minute gas bubbles at the electrodes) and for direct analysis of oxygen.

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[1] *J. Sci. Inst.*, 1939, *16*, 317. The authors thank Prof. A. Hartridge for assistance from this article.

The original apparatus of Reeve[1] is shown in Fig. 1 (XVIII³). It consists of a calibrated, uniform fine-bore capillary tube BAP, bent as shown. The U-shaped portion L was employed as a gas siphon and is drawn off to a fine point, which normally dips a few millimetres below the surface of the mercury in the jar C.

The straight portion HE is about 40 cm. in length, the remaining dimensions can be judged from the diagram, which is roughly to scale. The bore of the capillary used was such that 1 mm. length of the tube represented 0·000547 ml.; *i.e.* a bore of approximately 0·8 mm. The tube is provided with a rubber connecting-tube, a small reservoir of mercury, and a screw clip (these are not shown in figure); G is a jacketing tube which in the analysis of hydrocarbons was filled with amyl alcohol vapour. It may also be used, if necessary, as a constant-temperature water jacket. Normally the jacket was left empty, all measurements being carried out at room temperature. Three small, drawn-out bulbs E, F, and W (internal diameter about 3 mm. and volume about 0·05 ml.) are blown at the position shown. The jacketed portion of the tube, in which the actual measurements are carried out, was provided with a glass scale. Finally the whole apparatus is mounted on a suitable stand (not shown in sketch).

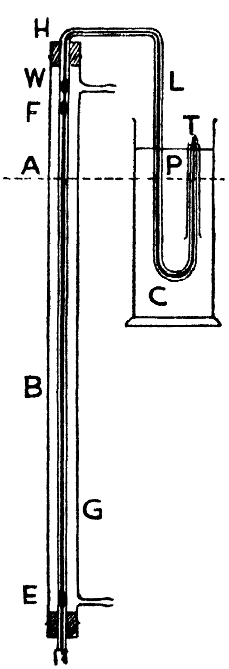

FIG. 1 (XVIII³)
The Reeves fine-bore capillary tube with jacket—showing siphon arrangement leading to trough

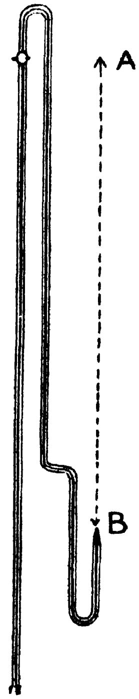

FIG. 2 (XVIII³)
The Reeves tube showing small explosion bulb

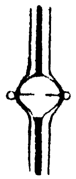

FIG. 3B (XVIII³)
By raising the mercury reservoir in the Reeves apparatus until mercury begins to enter the bulb at the bottom

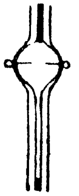

FIG. 3A (XVIII³)
Explosion bulb with mercury just entering bulb at top

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[1] *J. Chem. Soc.*, 1924, *125*, 1948.

The method of using the tube is as follows: The gases to be measured are collected from a Topler pump and stored over mercury in a small collecting-tube, about 7 cm. long, the closed end being drawn out somewhat. This collecting-tube is transferred in a crucible of mercury to the jar C, and the gas, with a following thread of mercury, is completely sucked into the measuring-tube in the usual manner. The thread of gas AB is now brought to the atmospheric pressure by bringing A to a point, found by trial to be proper, slightly above that indicated in the diagram, then removing the jar C, and adjusting the reservoir to bring A and P to the same level. The volume of gas is now read. Any slight error on levelling A with P is allowed for by calculation. The gas is now returned to its collecting-tube by reversing the above manipulation and then taken back and remeasured. If the mercury and apparatus are clean the two readings will not differ by more than a division (0·00027 ml.) in the case of gas samples of the order of 100 divisions (cap. 0·005 ml.). In the case of very small samples (order of 10 divisions = 0·005 ml.) the volume was read off to an estimated tenth of a division by using a lens. For explosions under reduced pressure a special tube was used. It consists of a small fine-bore capillary-tube, bent as shown Fig. 2 (XVIII[3])), and provided with the usual gas siphon. The length AB is 50 cm. and the remaining dimensions can be judged from the drawing, which is again roughly to scale. Near the top of the straight arm of the tube was blown a small bulb of about 0·03 ml. capacity, through the walls of which passed two platinum electrodes. It was found to be inconvenient, although not impossible, to use the mercury as electrodes for this bulb. A mercury reservoir was connected, by means of a rubber tube with screw clip (not shown in the diagram). The gas to be sparked was drawn into the tube in the usual manner and as it reached the bulb its pressure was reduced and it expanded to about four times its volume at atmospheric pressure. The result was that it could be sparked with ease, nor was there any loss of oxygen. The maximum volume of gas which could be sparked in this apparatus, used as described above, was 15 divisions (about 0·0075 ml.) measured at atmospheric pressure. This meant that as small a quantity as 2 divisions (0·001 ml.) of carbon monoxide or hydrogen could be detected and measured with some degree of accuracy. The apparatus could be used, however, for sparking larger volumes than 15 divisions by placing a rubber stopper over the point of the gas siphon, with the mercury reservoir in such a position that the mercury was just entering the bulb at the top (Fig. 3A (XVIII[3])). By then raising the mercury reservoir until mercury began to enter the bulb at the bottom (Fig. 3B (XVIII[3])) the gas was put into the correct position for sparking. It could not, of course, be completely burnt while some of it was still in the capillary owing to the well-known effect of such tubes of retarding explosion. The above explosion tube could be incorporated with the measuring-tube of Fig. 1 (XVIII[3]) thus making one single piece of apparatus for measuring the gases, &c.

Reeve's apparatus has been modified by Blacet and Volman[1] and extended to include a new procedure for the combustion of gases. This procedure has been applied in the analysis for nitrous oxide and also of methane and it presents the possibility of application in the case of several other gases. They employ a glass capillary tube calibrated in volumes throughout a suitable proportion of its length. Into this the dry gas is introduced and its initial volume measured. Small quantities of solid reagents are now introduced one at a time on the ends of short lengths of platinum wire. After each reagent has been brought into contact with the gas, its volume is re-measured.

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[1] *Ind. Eng. Chem. Anal.*, 1937, *9*, 44.

Blacet and Leighton [1] used a calibrated capillary 0·5 mm. diameter and 45 cm. long (corresponding to a volume of 0·112 ml.) with a water jacket (Fig. 4 (XVIII[3])). It is fitted at the base with a closed rubber tube. By compression the last traces of gas can be removed from the capillary by means of a small screw clip. The capillary tube is bent as shown, and is fitted under the gas holder H. The tip of this capillary is ground and fire-polished to a radius of curvature somewhat less than that of the top of the gas holders H and J. The lower end of the burette is sealed to a larger tube containing a trap to ensure the exclusion from the capillary of impurities and solid material which may be introduced in the sealing process. To the bell-shaped lower end is attached a short length of very heavy rubber pressure tubing. In setting up the burette it is first inverted and filled completely with mercury and a plug sealed in the free-end of the pressure tubing. When in position for use, the rubber tubing fits in the jaws of an especially heavy burette-clamp equipped with a finely threaded screw B. By means of this screw the mercury level in the burette can be changed with precision. By means of the telescoped brass tubes C and D and the machined screw E, equipment on the table F can be moved up or down with perfect control. G is a mercury reservoir of 7 cm. diameter, H and J are the containers for the gas samples and are also used for the processes of absorption and explosion. They have a capacity of approximately 2 ml. each.

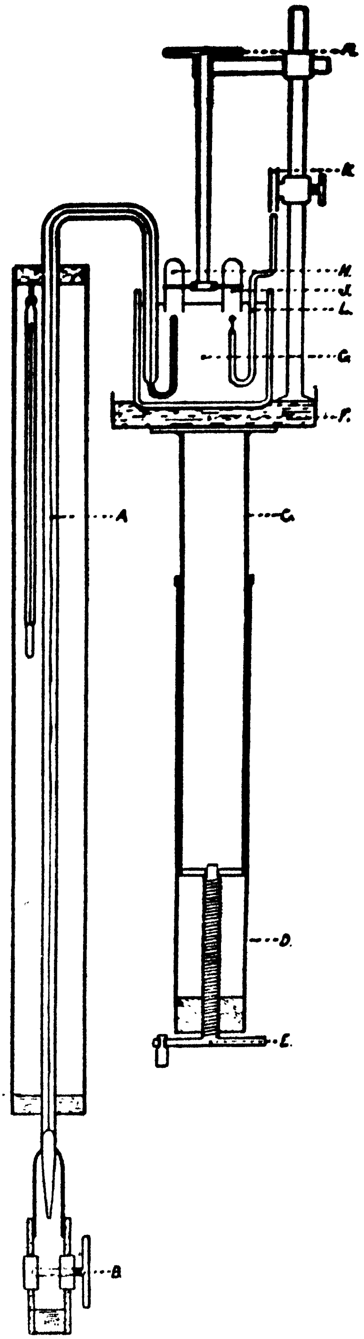

FIG. 4 (XVIII[3])
The Blacet and Leighton micro-gas analysis apparatus

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[1] *Ind. Eng. Chem. Anal.*, **1931**, *5*, 266.

In the diagram only two of these are shown, but, in fact, four of them are symmetrically attached by means of circular steel springs to the revolving table M. K is a brass tube which acts as a guide for accurately placing and supporting an absorbent holder L.

Solid reagents are employed; yellow phosphorus has been used to remove oxygen, fused potassium hydroxide to remove carbon dioxide and fused phosphorus pentoxide to remove water vapour. These absorbents were used also in the analysis by combustion of hydrogen, carbon monoxide, and methane. The results of the analysis of a number of different samples indicate that the degree of precision to be expected by this method is of the same order of magnitude as that ordinarily attained in microanalysis of gases.

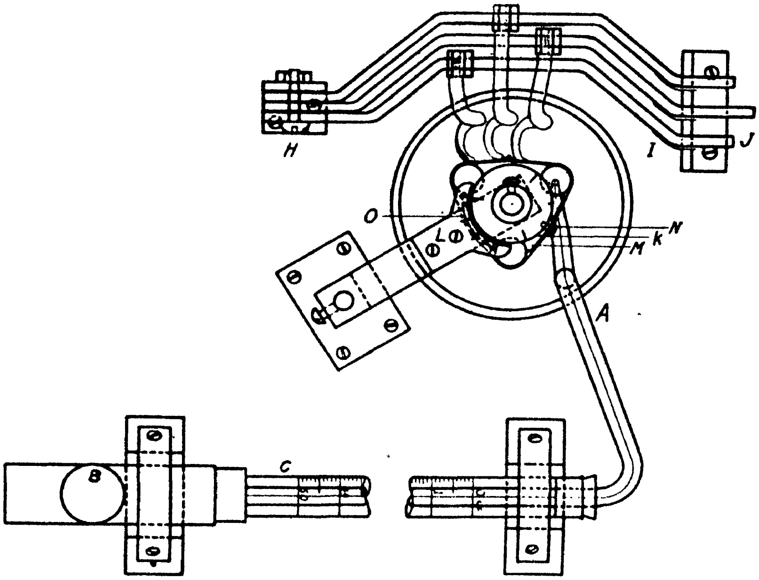

FIG. 5 (XVIII[3])
Plan of modified apparatus of Swearingen, Gerbes and Ellis

The Blacet–Leighton apparatus has been used by Le Roy and Steacie [1] to determine nitric oxide in a mixture of hydrogen, combustible gases or nitrogen. The absorbent was alkaline sodium sulphite with which it forms sodium hyponitrososulphate. A pellet of potassium hydroxide is ground in a mortar and sodium sulphite crystals ($Na_2SO_37H_2O$) are added till a thick paste is formed. No added moisture is necessary and if sufficient sodium sulphite is added very little drying is required—it should not be completely dried. Nitric oxide absorption is complete in 5 minutes. This reagent is superior to ferrous sulphate but the rate of absorption much slower.[2]

Usually the calibrated capillary-tube is vertical and mercury is the confining agent employed, but modifications have been described by

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[1] *Ibid.*, 1944, *16*, 341.

[2] Moser and Herzner, *Z. analyst.*, *Chem.*, 1924, *64*, 81.

Swearingen, Gerbes, and Ellis.[1] The method is similar in principle to the above, and of the same order of accuracy, but a different type of mechanical arrangement is used. A horizontal burette surrounded by another burette with a graduated scale is employed. The outer tubing acts as a water jacket. The horizontal burette has a separate mechanism attached so that it can be rotated for transferring gas. A plan of this apparatus and setting is shown in Fig. 5 (XVIII^3) drawn to scale. The parts are mounted on a moderately heavy board, such as 1·25 × 12 in. × 2·5 ft. which stands on rubber-headed tacks for legs to prevent sliding on the table. The diagram shows the top view of the levers, each carrying a bead support. The glass supports are curved so that their proximity to each other does not interfere with their motion about the centre at H. A thin sheet of brass is soldered to the lever at I to give friction. Obviously the solid reagent or bead must be placed in the gas with some precision: it must be well up into the gas space but must not touch the top of the tube. If the levers had been made straight, and rotary motion about the line HJ, as by twisting at J, while adjusting the position of the bead, would make this adjustment more difficult and inaccurate in the event that the bearing at H was not well fitted. To reduce this effect the levers are bent as shown to bring the bead nearer in line with the movable end J and the pivot H.

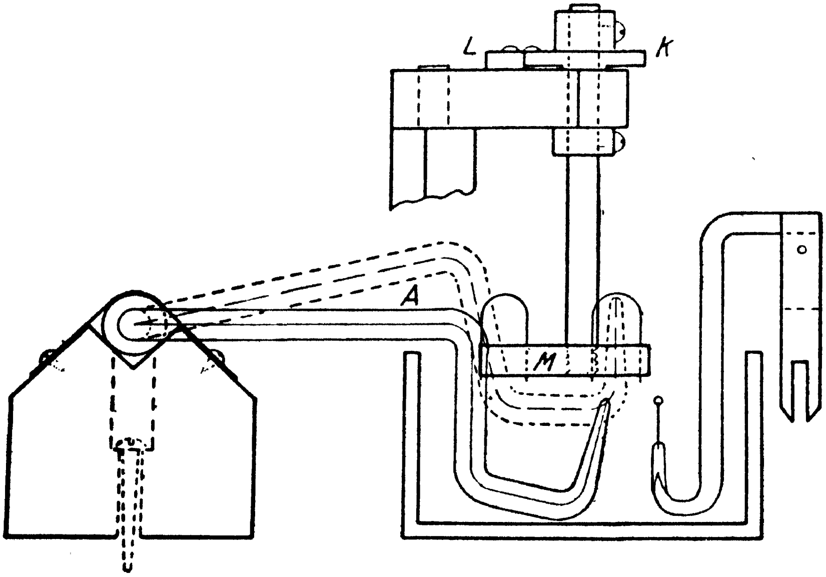

FIG. 6 (XVIII^3)
Right end view of micro-gas analysis apparatus

The tip of the burette is raised up into the gas containers by rotating the whole burette about its axis. This motion is conveniently and accurately produced by movement with the fingers at A, better shown in Fig. 6 (XVIII^3). The distance from the centre of rotation to the tip is about 4 in. (10 cm.) so the lateral motion here is only about 0·03 in. (0·07 cm.). The diameter of the burette is determined by balancing two opposing factors. If a gas sample is large too much time is required for reaction and, if small, too fine a capillary must be used for the burette with consequent excessive sticking of the mercury. Probably the optimum dimensions would require a capillary 0·5 to 0·7 mm. in diameter. Capillary-tubes are generally far from uniform in cross-section and must be calibrated carefully.

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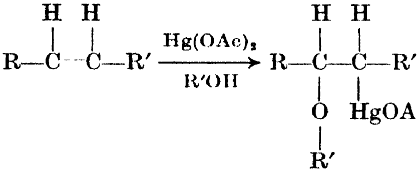
[1] *Ind. Eng. Chem. Anal.*, 1933, *5*, 369.

The graduated cylinder of a 50-ml. burette serves for the glass protecting-tube C. It furnishes easily readable uniform graduations as well as an air jacket for thermal protection. A large water jacket may be used but it is generally unnecessary for analyses of short duration. Gas samples are stored and transferred by means of suitable capillary-pipettes, having the same ground tip and shape as the bent portion of the capillary-burette with one change. The capillary-pipette comes up 1 in. (2·5 cm.) higher than at A, Fig. 6 (XVIII[3]), and is then bent down and enlarged for a short distance to give the necessary volume. The operation of the pipette is similar to that of the burette.

The aim has been to obtain a micro-method which can be used easily and rapidly and with the same order of accuracy as the standard macro-methods.

The Blacet–Leighton gas analysis apparatus, as modified by Blacet, MacDonald, and Leighton,[1] may be used for the analysis of gaseous olefines. Sintered-glass-heads with fuming sulphuric acid are employed. A more satisfactory method has been developed by Pyke, Kahn, and LeRoy,[2] using mercuric acetate to react with the olefines to form mercurials. In an alcoholic solution the following reaction occurs



$$\mathrm{R{-}\overset{\displaystyle H}{\overset{|}{C}}{=}\overset{\displaystyle H}{\overset{|}{C}}{-}R'} \xrightarrow[\mathrm{R'OH}]{\mathrm{Hg(OAc)_2}} \mathrm{R{-}\overset{\displaystyle H}{\overset{|}{\underset{\underset{\underset{\displaystyle R'}{|}}{\displaystyle O}}{\underset{|}{C}}}}{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle HgOAc}{\underset{|}{C}}}}{-}R'}$$

In aqueous solution the corresponding mercurial is formed. Since both types of mercurial are relatively nonvolatile, the method would appear to be satisfactory. In the case of the alkoxy derivatives, a nonvolatile alcohol must be chosen which does not dissolve paraffins to any appreciable extent. On the other hand, water is satisfactory because of its small affinity for paraffins and the fact that it can be readily removed from the remaining gas with fused potassium hydroxide or phosphorus pentoxide.[3] A more serious difficulty is the slowness of the reaction in most cases, although this can be overcome by the use of catalysts.[4, 5] In the analysis of ethylene-ethane mixtures trifluoride ethyl etherate was used as a catalyst and ethylene glycol for the alcoholic solution. A paste was made from 3 ml. of powdered mercuric acetate and 2 ml. of a 1 per cent solution of boron trifluoride-ethyl etherate in ethylene glycol and was then applied to the standard platinum loop adsorbent holder.

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[1] *Ind. Eng. Chem. Anal.*, 1933, *5*, 272.

[2] *Anal. Chem.*, 1947, *19*, 65.

[3] Blacet and Leighton, *Ind. Eng. Chem. Anal.*, 1931, *3*, 266.

[4] Birks and Wright, *J. Amer. Chem. Soc.*, 1940, *62*, 2412.

[5] Wright, *Ibid.*, 1935, *57*, 1993.

An improved capillary method has been developed by Sutton, Amber, and Dudley Smith.[1] Sutton's technique [2] will be described. His apparatus is shown in Figs. 7 (XVIII^3) and 8 (XVIII^3). He has found it desirable

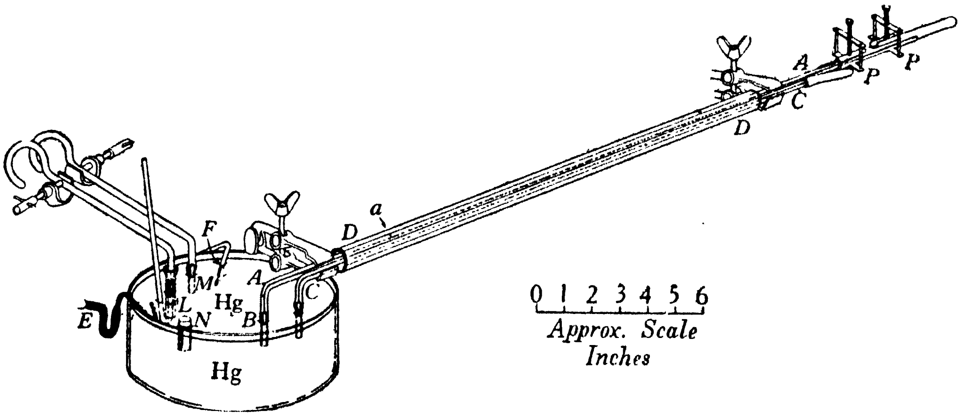

FIG. 7 (XVIII^3)
Sutton's micro-gas analysis apparatus

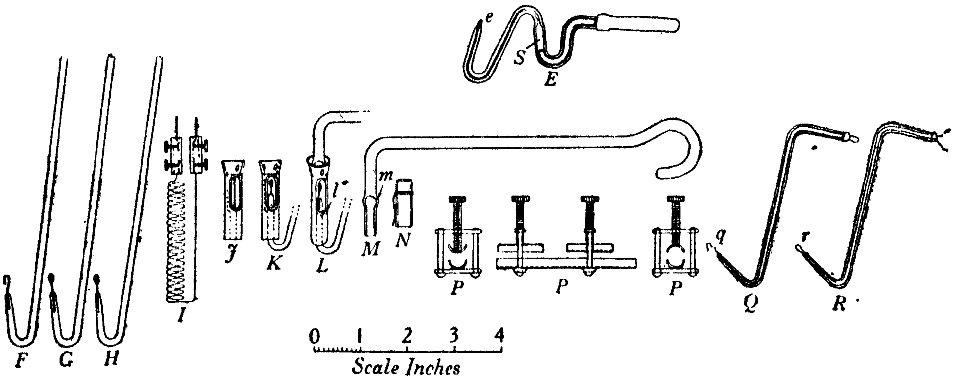

FIG. 8 (XVIII^3)
Fittings for Sutton's micro-gas analysis apparatus

(1) to keep the sample in one vessel BAA throughout the analysis and to bring the reagents to that vessel, thus avoiding any risk of loss of gas; (2) to employ a carefully shaped steel guide J to bring the reagents into position without soiling the walls of the reaction-chamber and without gas-lock or introduction of air; (3) to devise a holder E for storing the sample and for adding or transferring gases to the reaction chamber; and

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[1] *Catalogue of Ann. Exhib. Phys. Soc.*, 1936.

[2] *J. Sci. Inst.*, 1938, *15*, 133, and private communication from author. This paper gives a large number of references to premier work on the capillary method of micro-gas analysis.

(4) to include a device Q for carrying out those hot wire[1] reactions which are frequently employed in macro-analysis. (A similar device has since been described by Blacet and Volman.[2]) In addition, much of the apparatus used by earlier workers has been considerably modified by Luke.[3] Luke makes J of glass, and uses a straight wire, platinum gauge 44, in place of *q*. The two supports of this wire are brought through Q; their dimensions should ensure that the mercury does not rise sufficiently in temperature for oxidation to occur.

The measuring-chamber is a fine horizontal capillary tube AA, 0·5 mm. in diameter and 2 ft. long, one end of which is expanded and fused to a wider short tube B, about 4 mm. in diameter, which is used as the reaction chamber. This tube, together with a compensating tube CC, is placed within a wide glass tube DD which acts as an air-jacket to the two tubes. The measuring-chamber AA should be calibrated; it may either be graduated along its whole length, or one reference line, *a*, may be placed upon it and the graduations placed round the jacketing tube DD; the latter method has the advantage that the graduations are on the outside of the apparatus and can be seen clearly. The reaction chamber dips into a wide bowl Hg containing mercury. The end of AA remote from the reaction chamber is fitted with a rubber cap by means of which mercury may be drawn into the capillary system; PP is a convenient screw fitting for making fine adjustments.

Inverted specimen tubes N or the glass vessels M make convenient reservoirs for reagents and for the gas to be analysed. To transfer a sample of gas from M to B, use is made of a small glass vessel E drawn to a tip at one end and fitted with a rubber cap at the other. E is filled with mercury, the tip is then placed in the mercury bath, the cap squeezed between the fingers so as to expel any trace of air and about 0·5 ml. of mercury, the tip is then passed through the mercury into the gas in M, the pressure of the fingers is lessened and a sample of gas drawn into E, the tip is immersed again in the mercury and the pressure removed, mercury being drawn into E and completely isolating the sample of gas. The tip of E may then be passed into the mercury-filled reaction chamber B and a sample of gas of the desired magnitude forced into it. On removing E, the screw PP is adjusted so as to draw this sample into the measuring-tube AA.

To ensure that the meniscus of the mercury column affects the pressure in the gas column to the same extent, each measurement in AA is preceded by a short repeatable routine. By unscrewing PP the gas is drawn into AA just beyond the fixed mark *a*. PP is then screwed down slowly until mercury begins to move into B and the meniscus approaches *a*; this occurs when the excess pressure in the gas column just exceeds the resistance of the meniscus when at *a*. A sample 25 cm. in length will give a consistency of 1 in 400 provided the tube is clean.

In common with other forms of "constant-pressure" apparatus, the required volume measurements are merely relative, and it is sufficient to compare at each stage of the analysis the length of the sample with that of a sample of dry air in the tube CC ; the latter indicates any significant change in temperature, in atmospheric pressure or in the relative positions of the measuring system and of the mercury reservoir Hg. In practice, it is convenient to compensate for these changes of temperature and of pressure, if any, by using the vessel E to adjust the level of mercury in the reservoir until the air sample occupies its original position.

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[1] Ambler, *Analyst*, 1929, *54*, 517; 1930, *55*, 436 and 677; 1931, *56*, 635; Lunge-Ambler, *Technical Gas Analysis*, p. 128 (London: Gurney & Jackson, 1934).

[2] *Ind. Eng. Chem. Anal.*, 1937, *9*, 44.

[3] Private Communication.

Solid reagents are held by a platinum loop such as that at F, and may be fused by holding the loop within the electrically heated coil I. A gas flame is not practicable, since the gas and the products of its combustion may react with the material to be fused. In G and H, the loop is filled with a porous mixture of kaolin and ground porcelain,[1] made coherent by holding in a flame ; the air in the pores may be replaced by a liquid reagent contained in M or N, by merely passing the loop into the liquid for a few seconds. When not in use the loops may be stored inverted under mercury as at F.

J is a carefully shaped steel tube essential for clean manipulation without risk of soiling the reaction chamber B. It is placed over a reagent rod as at K, and if the sections are somewhat elliptical, a slight rotation will fix it there. As the lip of J is wide, the system K may readily be placed around the bottom of either a reagent container M or the reaction chamber B, and being conical, it will guide the reagent rod directly into the centre of M or B. The enlargement *m* ensures that a passage *l* is maintained, without which traces of air may become entrapped within J and forced into M or B.

' Hot wire ' reactions may be obtained by placing within B the end of Q ; the flexible platinum wire *q* then forms automatically a loop passing through the gas in B and into the mercury below : an electric current may thus be passed through the mercury column within Q, through *q* and through the mercury in the reservoir. By placing the end of R within B in a similar manner, sparks may be passed through the gas.

The quantity of reagent required to complete an absorption is very small ; it is desirable that the amount used should also be small as the surfaces of mercury and of glass may become soiled if an unnecessary excess is present. The proportion of sample lost by so-called ' physical ' solution is considerably less when the reagents are held by the porous beads than when the sample is shaken with excess reagent in the manner that has been customary hitherto. Gas is seldom added or removed with the beads ; in the rare cases when this does occur, the amounts are relatively large and do not escape detection. The limit of accuracy set by the apparatus, therefore, depends mainly on the reliability of the readings of the lengths of the columns of gas in the capillary-tube AA. This in turn depends upon the nature of the tube and its cleanliness ; it is useful, therefore, to dry the sample before each measurement by introducing into it a bead of solid phosphorus pentoxide. With the actual apparatus in use, readings can be repeated to 1/400th part of the initial volume and no further refinement has been attempted.

It is for these reasons that the percentage composition of a sample of 0·2 ml. can be measured in the micro-apparatus with the same order of accuracy as the percentage composition of a larger sample of 20 ml. to 100 ml. can be measured in one of the several types of apparatus employed for the general analysis of a mixture of gases, such for example as flue gases.

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[1] Swearingen, Gerbes, and Ellis, *Ind. Eng. Chem. Anal.*, 1933, *5*, 369.

Note on the Drying of Gases. For the drying of gases various chemical substances may be employed. The actual substance used depends on various factors : selective action, effectiveness, permanency in structure of the substance on continued use, rapidity of action, power of regeneration, &c. Among the usual substances employed are anhydrous calcium chloride, phosphorus pentoxide, concentrated sulphuric acid, potassium hydroxide, magnesium perchlorate, silica gel, &c.

Calcium Chloride. For general uses calcium chloride is generally employed. It should be free from free calcium oxide. It is stated that calcium chloride absorbs traces of carbon dioxide. The vapour pressure of calcium chloride at 20° is about 0·3 mm. so that this substance will not remove the last traces of water from gases. Dittmar and Henderson found that air dried by calcium chloride still contained about 0·001 gram of moisture per litre of air. It is, however, a very good substance for preliminary drying to be followed by phosphorus pentoxide or some more highly efficient drier.

Phosphorus Pentoxide. This substance is generally regarded as the most active drying agent. It reduces the water content of gases to very small amounts. Drying by phosphorus pentoxide, especially with repeated circulation through the desiccating agent and allowing the gas to stand in contact with the phosphorus pentoxide, is the most efficient method of drying. By this means of intensive drying the fraction of water molecules can be reduced as low as 10^{-10}. The ordinary laboratory reagent often contains traces of phosphorus trioxide. This latter impurity should not be present in the drying reagent as it may reduce water with the formation of hydrogen. It can be detected by acting on the phosphorus compound with silver nitrate or mercuric chloride and if the trioxide is present these salts are reduced. Phosphorus pentoxide, free from phosphorus trioxide, for gas analysis can be purchased.

Concentrated Sulphuric Acid (purified). This is an exceptionally good absorbent for water. It can decrease the water content of gases at ordinary temperatures to about 10^{-2} mm. Air dried by sulphuric acid has been found by Dibbitts to contain a trace of moisture (0·002 mg. of moisture per 100 litres of air.)

Potassium hydroxide (pure) is also a good absorbent.

Magnesium Perchlorate. While more convenient to handle than phosphorus pentoxide it is not as efficient as this substance. It can be used like calcium chloride and backed by phosphorus pentoxide. Various salts are employed, e.g. the anhydrous salts and the trihydrate. They both readily absorb water and ultimately give the hydrated salt with six molecules of water. The perchlorate tends to become liquid on prolonged use and is not readily regenerated without removal from the drying-tubes. ‘ Dehydrite ’ is the trihydrate. ‘ Anhydrone ’ is the anhydrous salt. The barium salt—‘ Desicchlora ’ is also used as an absorbing agent. These salts are granular and are easier to handle than the magnesium perchlorate.

Silica Gel. This reagent acts differently from the others outlined. It acts as an adsorbent rather than as an absorbing reagent. It is not suitable for water vapour in quantitative work when other substances such as hydrocarbon vapours, acetone, benzene, &c., are present. These also would be adsorbed at the same time. The efficiency is lowered when the silica gel adsorbs about 20 per cent of water.

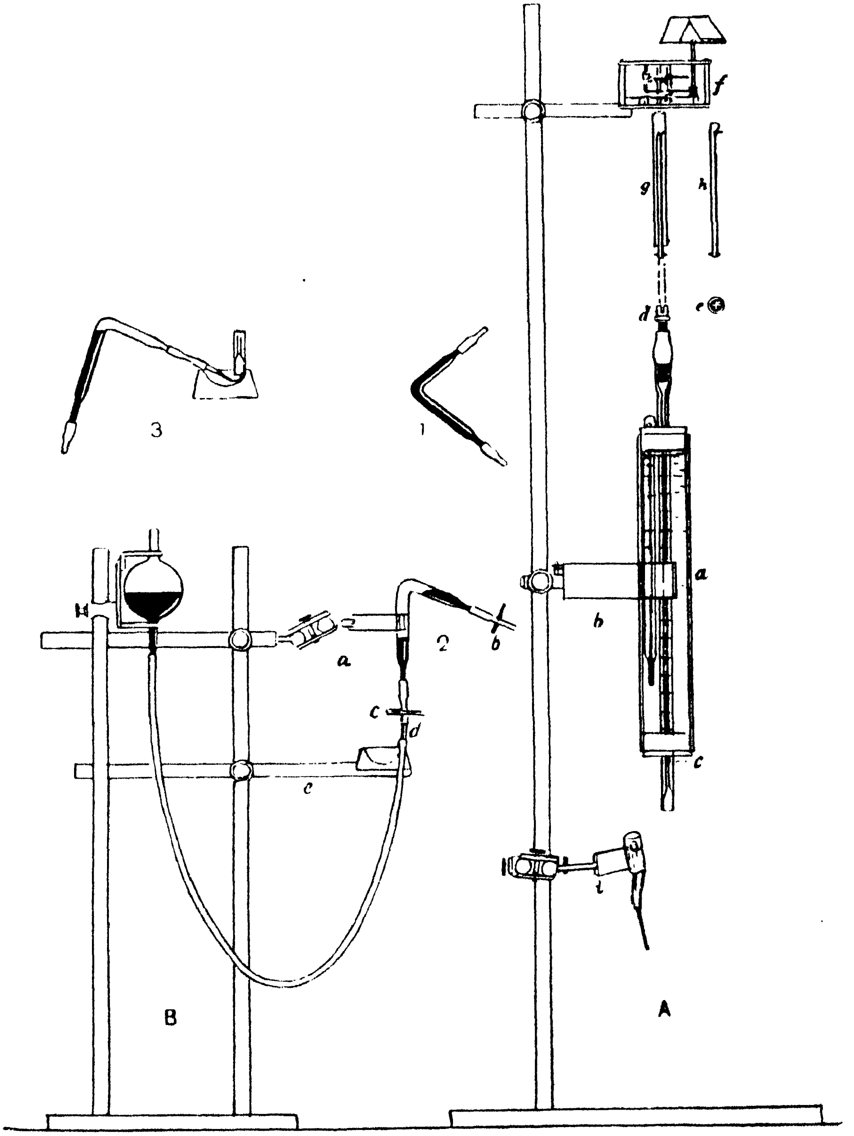

FIG. 9 (XVIII^{8})
The Schmit-Jensen micro-gas analysis apparatus

(*b*) Moist-Gas, Variable-Volume Method

In this method, the confining fluid is either mercury or some other fluid; fluid reagents are employed and the gas in capillary burettes is measured either saturated, or partly saturated, with aqueous vapour. This method is suitable for the analysis of 1 to 20 cu. mm. of such mixed gases as carbon dioxide, carbon monoxide, hydrogen, oxygen, and nitrogen (or inert gases).

Microscopic methods for gas analysis were published by Krogh [1] in 1908. One of these was based on the fact that small air bubbles placed in a fluid behave much as semi-fluid fat drops, and easily allow transport from one place to another without disunion. For analysis an air-bubble is sucked into a capillary-tube of uniform calibre about 0·25 mm. in diameter and measured. A length of 100 mm. corresponds to a volume of approximately 5 cu. mm. Gas absorptions are next performed one after the other in a funnel at the lower end of the capillary-tube. Each adsorption process being completed the air bubble is drawn into the capillary and remeasured. When Schmit-Jensen [2] used the method about 1916 he found that the experimental technique was difficult and satisfactory results could not readily be obtained on micro-quantities. He improved the method and obtained an accuracy of 0·1 per cent.

The modified apparatus shows an increase in the diameter of the capillary-tube to about 1 mm. The capillary-tube is 100 mm. in length corresponding to a volume of 85 cu. mm. These modifications allow air-bubbles so big, that it is possible to insert a platinum wire for combustion analysis. The thickness of the film of water adhering to the inside of the capillary-tube depends greatly upon the speed at which the air-bubble is moved upwards. This is effected by means of clockwork. Schmit-Jensen's apparatus is shown in Fig. 9 (XVIII^3). The following list explains the various parts of the apparatus :

A. Arrangements for Micro-analysis

a, capillary-tube with water jacket and thermometer ;
b, clamp and bosshead with arrangement for stopping in vertical position ;
c, division taken as zero in measurement ;
d, vulcanite screw with brass top ;
e, screw seen from the top with cruciform incision of the brass top ;
f, clockwork with wings for regulating the speed ;
g, metal tube fixed to the axle of the clockwork, containing a movable iron-pin to fit incision of *d* ;
h, iron-pin alone ;
i, combustion funnel, carried by a clamp (compare B,*a*) adjustable to any angle. The conduction wires connect the platinum wire with accumulators and rheostat.

B. Stand for Micro-receivers

a, elastic clamp with double ball-and-socket joint for fixation of micro-receiver ;
b and *c*, clips on india-rubber tubing of micro-receiver ;
d, piece of glass tube for disconnexion from mercury reservoir ;
e, clamp holding square glass pot with excavation for special glycerine mixture [3] for immersion of the absorption funnel of A,*a*.

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[1] *Skand. Arch. Physiol.*, 1908, *20*, 279, and *Abderhalden. Biochem. Arbeit.*, 1915, *8*, 495.

[2] *Biochem. J.*, 1920, *14*, 4.

[3] Owing to the difficulty of preventing rapid diffusion of carbon dioxide and other gases Schmit-Jensen recommends filling the funnel with a special liquid. It consists of a saturated solution of sodium chloride mixed with an equal amount of glycerine and made acid with hydrocloric acid.

1, position 1 of receiver, being used when the receiver has to be filled with mercury or when the last gas has to be driven out of the shorter limb for analysis;

2, position 2; gas has just been sucked in, receiver clipped at both ends and levelling-tube raised again;

3, position 3; gas from the longer limb is driven out through a narrow curved glass cannula into the absorption funnel, immersed in 'the special glycerine mixture' *e*. A drop of mercury regularly left in the drawn-out part of the shorter limb is pushed in front of the gas, so removing any foreign gas present.

It is possible by means of this apparatus to estimate carbon dioxide and oxygen by absorption, hydrogen and methane by combustion in a given air-sample of about 80 mm.[3] Methane may be estimated either by absorption or combustion according to circumstances. Inert gases are calculated as residue.

Fractional combustion of mixtures of hydrogen and methane is also practicable by means of this technique. The accidental error (standard deviation) in the present micro-analyses corresponds on an average to an error of 0·1 mm. The systematic error differs for the different gases. Scholander's technique for the analysis of small amounts (of the order of 1 ml.) of respiratory gases is described in Vol. 2, Chap. I, pp. 36–37.

A method of displacing mercury by means of a metal screw to the capillary-tube was used by Christiansen and Huffman[1] in their micro-method of gas analysis. Their method has not been widely adopted.

(*c*) Constant-volume Variable-Pressure Method

(1) Use of 'Diver'. In this method the confining liquid acts as a flotation medium for a small gas-containing vessel or 'diver', fluid reagents are employed and the gas may contain aqueous vapour. It was first used by Linderstrom-Lang[2] in 1937 and elaborated later by Boell, Needham, and Peters.[3] It can be used for the estimation of oxygen absorption and the output of carbon dioxide from living tissue.[4]

The tissue to be examined is placed in a 'diver' which consists of a small glass vessel, to which is attached a glass weight. At the upper end of this vessel is attached a glass tube by means of which reagents are introduced when required. Those used by Needham have a volume of 20–25 cu. mm. and the neck tubes a length of 7–12 mm. In the end of the neck tube is placed some potassium hydroxide for absorption of carbon dioxide which is evolved by the tissue leaving an air space. Some dilute acid is now placed in position, so that the carbon dioxide may be evolved again by mixing with the acid. Above the acid, again leaving an air space, is a 'piston' drop of acid and then an oil seal. In order to prevent a premature mixing of the reagents in the 'neck' tube of the diver, the interior of the tube is coated with wax.

The diver is now placed in a vessel containing a suitable flotation liquid, e.g. lithium chloride. A simple fluid manometer is attached to the vessel containing the diver, together with an adjusting mechanism for the pressure.

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[1] *Z. analyst. Chem.*, 1930, *80*, 435.

[2] *Nature*, 1937, *140*, 108.

[3] *Proc. Roy. Soc. B.*, 1939, *127*, 325.

[4] Hartridge, *J. Sci. Inst.*, 1939, *16*, 322.

This is adjusted so that the diver remains in unstable equilibrium roughly midway in the vessel. The pressure in the manometer is read from time to time. The variation of pressure that is observed is due to the absorption of oxygen by the tissue, since the carbon dioxide is absorbed by the potassium hydroxide in the neck of the diver. By applying considerable pressure to the whole apparatus, first the potassium hydroxide solutions, then the acids are driven down the tube into the main body of the diver, and carbon dioxide gas is evolved. On releasing the pressure, it is found that the buoyancy of the diver has been changed by the evolution of the gas. The pressure is again adjusted until the diver is once more in equilibrium, neither rising nor falling, and the new pressure is measured by the manometer. From the knowledge of the volume of the diver and other constants of the apparatus, and of the initial and final pressures, the oxygen absorbed and the carbon dioxide evolved by the tissue can be calculated.

The principle of the diver used for the purpose of an ultra-micro-manometer gives an instrument 1,500 times more sensitive than the Warburg manometer (*see* p. 515). The delicacy of the method can be judged by the statement of the authors [1] that whereas 1 cm. on the Warburg manometer scale corresponds to a gas change of about 20 cu. mm., 1 cm. on the diver manometer scale corresponds to a gas change of about 0·008 cu. mm.

The apparatus of Boell, Needham, and Peters [2] is given in Fig. 10 (XVIII^3) and shows a diver of the type used by them. The tissue and the physiological medium occupy the bottom of the diver bulb Fig. 11 (XVIII^3), beneath which there is a glass tail to maintain the diver in a vertical position. The amount of glass in the tail is adjusted so that the equilibrium pressure of this diver is fairly near that of the atmosphere. The neck is partly occupied by a drop of oil, so placed that there is a small bubble of air between the oil and the flotation medium. The flotation medium—a strong salt solution giving minimum gas solubility without excessive viscosity—is seen in Fig. 10 (XVIII^3) with the diver floating in it. The diver vessel is submerged in an accurately regulated thermostatic water-bath, and connected to a water manometer, the pressure in which can be adjusted (as in a Warburg manometer) by a syringe mechanism. It is convenient to have fine and coarse adjustments.

Compensation for changes in temperature and barometric pressure is carried out by means of a duplicate diver and manometer. The technique applied being the same, except that no tissue is placed inside the ' diver '.

The apparatus and duplicate are placed side by side in a thermostat. The buoyancy of the diver depends on the volume of gas which it contains. If the gas volume increases, the diver tends to rise, and vice versa. If, owing to an evolution or absorption of gas inside the diver, the volume of gas changes, then this causes the diver to move. But by altering the pressure inside the apparatus which contains the diver, the volume of gas in the diver can be brought to its original volume and the movement of the diver is thus averted. The method is then one in which the gas is brought to a constant volume. Deviations from constancy are indicated by a tendency of the diver to rise or fall and the pressure of the gas inside the diver at constant volume is measured by the water manometer. To take

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[1] *Loc. cit.*

[2] *Loc. cit.*

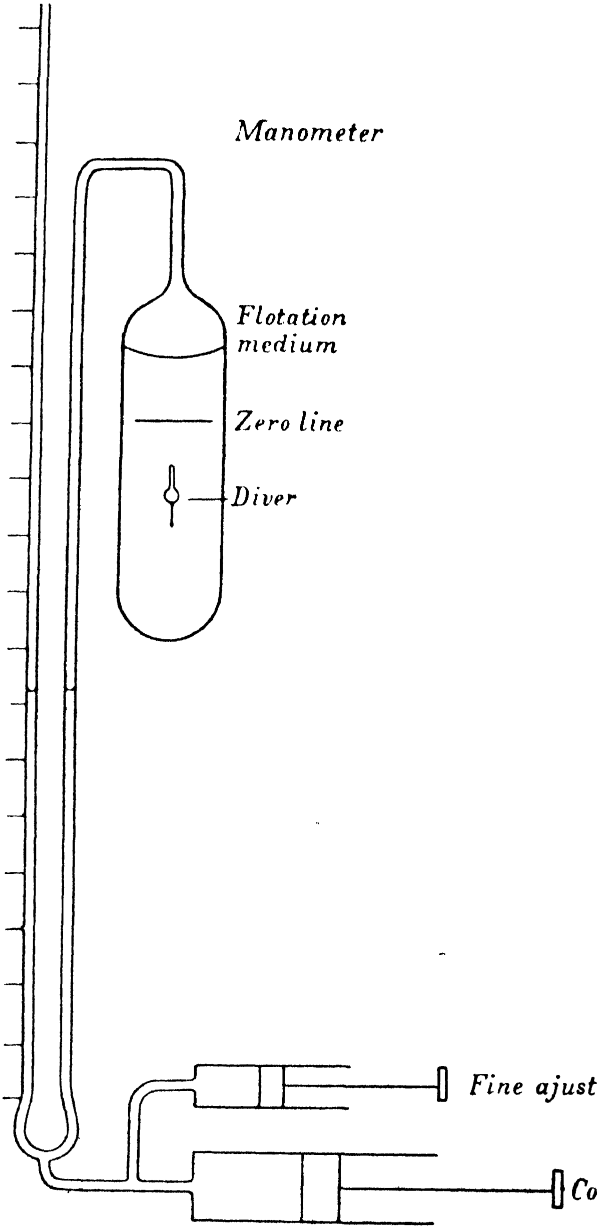

FIG. 10 (XVIII[3])
The diver apparatus of Boell, Needham, and Peters

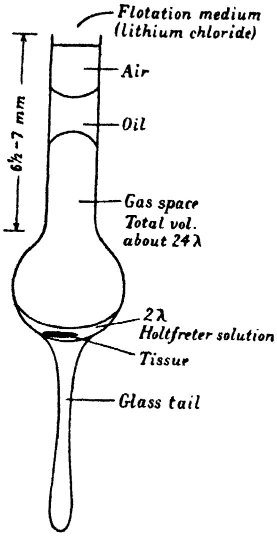
Flotation medium (lithium chloride)
Air
Oil
6½-7 mm
Gas space Total vol. about 24λ
2λ Holtfreter solution
Tissue
Glass tail

FIG. 11 (XVIII[3])
The diver bulb

a reading, it is only necessary to bring the diver to a temporary standstill at the zero line, and to note the pressure. It is possible to measure changes of the order of a millionth of a millilitre of gas.

(2) **The Langmuir Technique.** There is no confining fluid in this technique and the pressure of the gas is obtained by a manometric method.

The method was widely used before measurement in capillary-tubes was standardized and made accurate. Many designs of this type of apparatus first developed by Langmuir [1] have been made. They are usually elaborate and are built for a specific problem and require skill to operate and maintain. The gases are manipulated and passed over solid reagents at low pressurse with some type of vacuum technique. The volume is usually measured by differences in pressure with some form of McLeod gauge. Campbell [2] used an apparatus consisting of a large globe-shaped bulb with a hollow tube of very small capacity sealed to the base. At the top is sealed a glass tube which can be connected to the vacuum supply. Gas is introduced into the bulb at a recorded pressure and then the bottom capillary is surrounded in a freezing mixture so that condensation of the gases or vapours occurs. When the cooling agent is removed the pressure in the bulb increases. When condensation ceases the pressure will remain constant. A second gas with higher condensation value is then added, the experiment repeated, and a new pressure figure obtained. For method of calculation of analysis see Campbell's paper.[3]

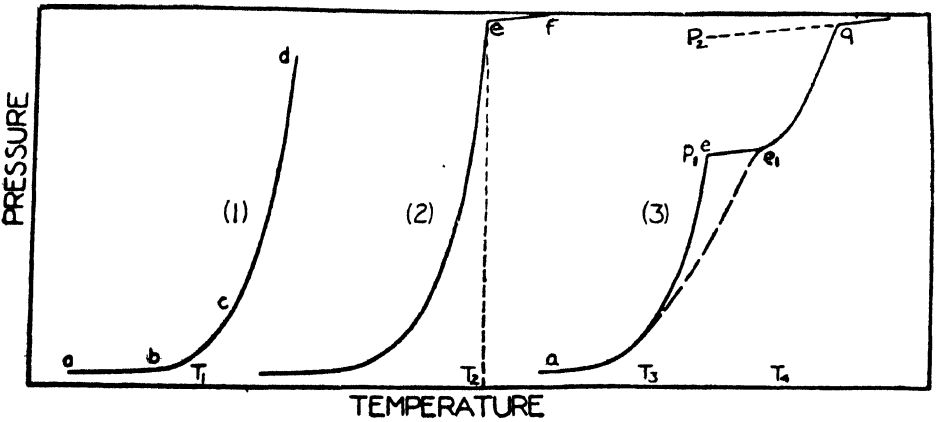

FIG. 12 (XVIII[3])
The pressure–temperature relationship between various gases under particular conditions

Sebastian and Howard [4] have applied this method successfully to the analysis of synthetic mixtures of pure hydrocarbons and other gas samples. Less than 1 ml. of gas (at N.T.P.) is required and it is not destroyed in the analysis.

For every gaseous compound there is a range of temperature over which the change of pressure with temperature is relatively rapid. The apparatus must be calibrated with mixtures of known composition. The time required for an analysis is 3–5 hours, and an accuracy of ± 1 per cent can be secured. The limitation of the method lies in the impossibility of determining in a mixture saturated and unsaturated hydrocarbons of the same number of carbon atoms. In this method it is usual to plot vapour pressure-temperature curves in linear form, log p : 1/T. If, however, p itself is plotted against the absolute temperature, a graph of the form shown in Fig. 12 (XVIII^3) curve 1, results. This portrays the relation in a closed system of one component when a vapour phase is in equilibrium with its liquid or solid phase. If the system is sufficiently large so that ultimately, owing to increasing temperature, the condensed phase disappears entirely, the curve takes the form shown in curve 2. The first portions of these curves are identical. If T_2 is the temperature at which the condensed phase disappears, the curve from e to f represents merely the expansion of the vapour ($p \propto T$), and because of the comparatively small rate of change of p with T under such conditions, the change in direction of curve 2 results.

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[1] *J. Amer. Chem. Soc.*, 1912, *34*, 1310; *see also* Ryder, *ibid.*, 1918, *60*, 1657, and Prescott, *ibid.*, 1928, *50*, 3237.

[2] *Proc. Phys. Soc.*, 1921, *33*, 287.

[3] *Loc. cit.*

[4] *Ind. Eng. Chem. Anal.*, 1934, *6*, 172.

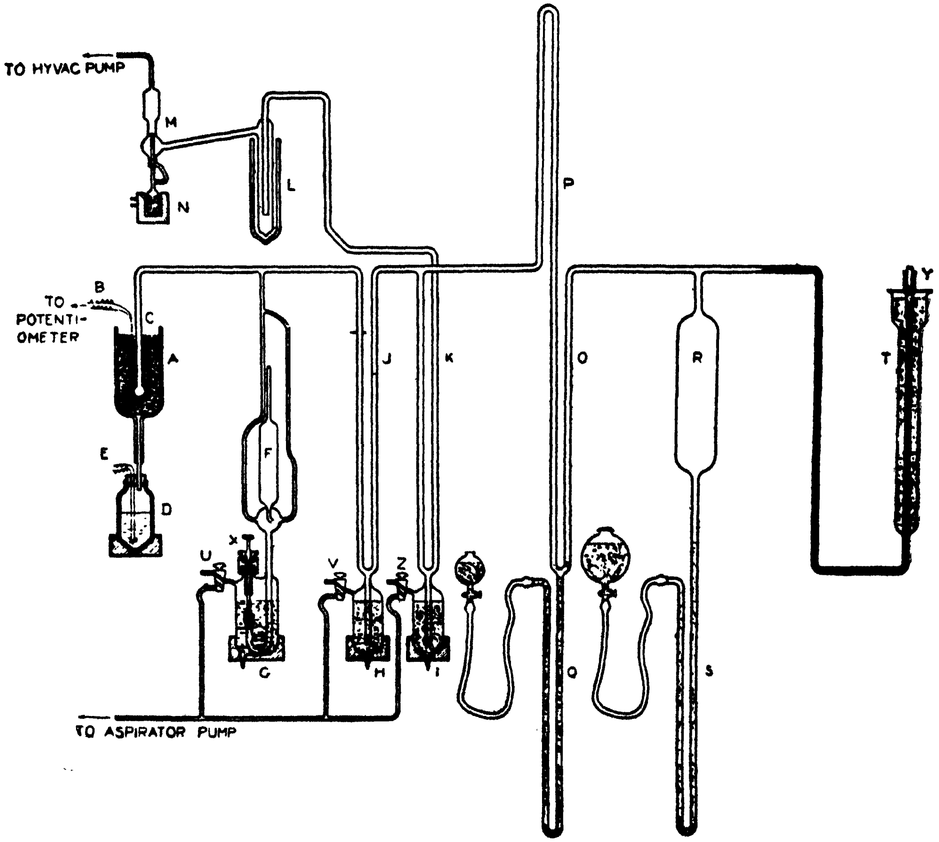

FIG. 13 (XVIII^3)
Apparatus for microanalysis of gaseous mixtures by pressure-temperature curves

If two substances form separate phases in the condensed state, and if their ‘ initial vaporization temperatures ’ are sufficiently far apart so that the more volatile will be evaporated relatively completely from the condensed phase before the vapour pressure of the second becomes appreciable, it is evident that a quantitative determination of the amount of each present can be made only by measurements of p and T, and plotting p against T.

The pressure-temperature relations in such a system will be as shown in Fig. 12 (XVIII[3]), curve 3. The initial vaporization temperatures T_3 and T_4 are characteristic of the components, and hence indicate the qualitative composition ; the ratio of p_1 to p_2 gives the fraction by volume of the more volatile component present in the mixture and hence permits calculation of its quantitative composition.

The general layout of Sebastian and Howard's apparatus is shown in Fig. 13 (XVIII[3]). The notation is as follows :

A. Dewar flask with vacuum-jacketed tube connexion.
B. Copper-constantan thermocouple in direct contact with freezing-bulb.
C. Copper-jacketed freezing-tube placed in a 2-mm. thick copper shield.
D. Lower Dewar flask containing liquid nitrogen.
E. Electric heating coil in series with rheostat and ammeter.
F. McLeod gauge.
G, H, I. Mercury reservoirs.
J, K, O. Mercury cut-off tubes with mark provided on J.
L. Liquid nitrogen trap.
M. Mercury vapour-pump backed by a Cenco Hyvac oil pump.
N. Electric heater.
P. Connecting U-tubes for introduction of sample.
Q, S. Mercury-filled U-tubes in connexion with levelling-bottles.
R. Expansion bulb.
T. Sampling reservoir.
U, V, Z. Two-way stop-cocks for connecting with atmosphere of suction.
X. Screw attachment connected with stopper for closing communication between reservoir G and McLeod gauge.
Y. Ground-glass stopper provided with cup for holding weights.

Fig. 14 (XVIII[3]) shows an analysis by Sebastian and Howard [1] of a synthetic mixture of carbon dioxide and *n*-butane.

	Composition as prepared	Analytical as found	Results on air-free basis
	Per cent	Per cent	Per cent
Carbon dioxide . . .	46·6	45·9	46·5
n-Butane	53·4	52·8	53·5
Air	—	1·3	—
	100·0	100·0	100·0

The total pressure in the system at room temperature was 0·2606 mm. and, after condensation, 0·2615 mm. These small pressures due to non-condensable gases appeared in practically all analyses. The curve [2] shows a rapid change in slope starting at 108° K. and continuing for approximately 12°. The flat portion in the curve, indicating complete evaporation of the carbon dioxide from the condensed phase, appears at a pressure of 0·110 mm. This is the pressure exerted by carbon dioxide plus non-condensable gas (assumed to be air) at this temperature. The volume percentage of carbon dioxide and air in mixture is given by the ratio of this pressure to the total pressure of the sample if it could be vaporized completely at this temperature. The value for the total pressure which would be exerted by the sample is obtained graphically by a straight-line extrapolation of the pT curve from the temperature at which the sample has completely evaporated down to the temperature in question. Such a straight-line extrapolation is, of course, not exact; however, except at low temperatures the errors introduced by its use have been shown to be negligible by a comparison of the results obtained by the use of this graphical extrapolation with those obtained when the extrapolation was made by the use of pT values for such gases as helium and nitrogen, which has been determined directly in the apparatus. The value for total p so obtained is 0·233 mm. Then $\frac{0{\cdot}110}{0{\cdot}233} \times 100$ or 47·2 per cent is carbon dioxide plus air. The butane must be $\frac{0{\cdot}233-0{\cdot}110}{0{\cdot}233} \times 100$ or 52·8 per cent. The air is calculated in a similar way, $\frac{0{\cdot}003}{0{\cdot}228} \times 100$ and found to be 1·3 per cent.

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[1] *Loc. cit.*

[2] Fig. 14 (XVIII[3]).

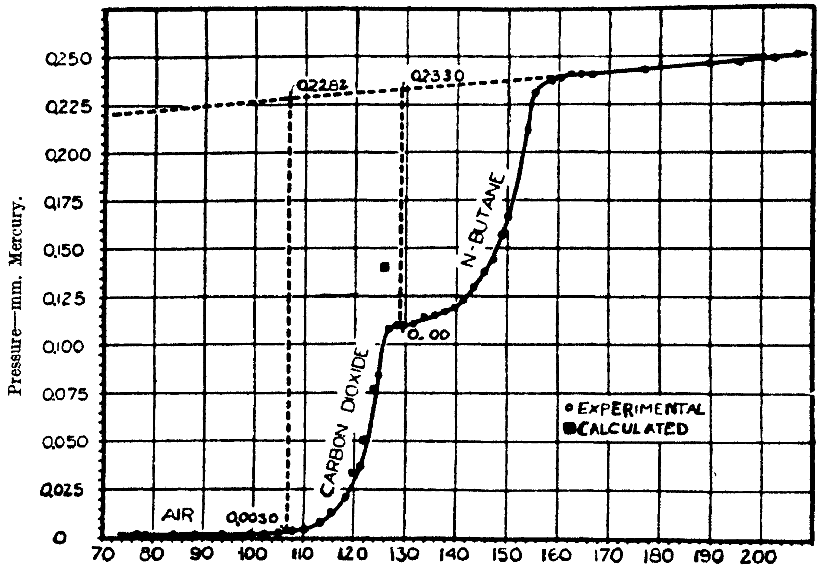

FIG. 14 (XVIII⁸)
Pressure-temperature relationship in a mixture of carbon dioxide, n-butane, and air

(3) **Use of Mica Membrane.** Another example of the variable pressure method is the so-called mica-plate technique of Heatley, Berenblum, and Chain.[1] The material to be examined rests in a completely closed chamber, one wall of which consists of a thin sheet of mica. The plane mirrors are attached to the latter and when the volume of the gas in the chamber changes the mica will bulge either inwards or outwards, with the

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[1] *Biochem. J.*, 1939, *33*, 53.

result the mirrors will tilt in the opposite directions. By applying a positive or negative pressure to the outside of the mica membrane the latter may be brought back to its original position, a simple optical system being used to detect when the mirrors are in the same plane. Then knowing the volume of the gas space and the change in pressure in it, the amount of gas absorbed or given out may be calculated.

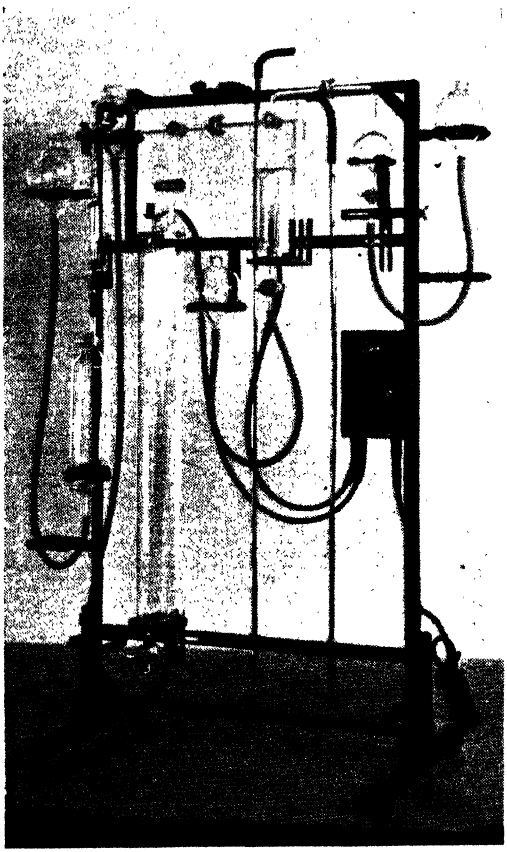

FIG. 15 (XVIII[3])
The butadiene gas analyser

The component parts of the apparatus are (1) The respiration chamber containing the tissue; (2) the metal case containing the chamber; (3) the optical system; (4) thermostat, with heaters, thermo-regulator, &c.; (5) the pressure-regulating mechanism and manometer and arrangements for filling the chambers with any desired gas mixture. The original papers should be consulted for details of these.

The respiration chamber consists of two slabs of glass 25 mm. square, one 3–4 mm. thick and the other about 2 mm. Connected to the cavities are little grooves, in each one of which a reagent may be placed. The thick slab has a cavity of 40 to 80 *μl.* in which lies the material to be examined. The chamber containing the tissue is drilled out of slabs of glass by means of a diamond drill.

As in Needham's 'diver' apparatus, the reagents are (I) potassium hydroxide solution, in order to absorb carbon dioxide gas evolved by the tissue, and (II) dilute hydrochloric acid. On mixing the potash solution with dilute acid, an immediate rapid evolution of carbon dioxide gas occurs. The mixing of the droplets of the reagents may be carried out by dragging a small steel ball from the groove containing one reagent to the groove containing the second reagent, by means of an electro-magnet, the poles of which are situated outside the gas chamber. The balls, about 1·5 mm. diameter, are given several coatings of bakelite varnish, each coat being stoved before applying the next coat. The balls are next coated with paraffin wax (melting-point 50°) the surplus wax being removed by hot filter paper. They are then coated with kaolin. The varnish and wax prevent the balls from rusting, and the kaolin enables them to be wetted and thus to move one reagent so that it may be brought into contact with another.

Method depending on a Chemical Reaction combined with a Volumetric Determination. For the estimation of butadiene in the presence of other olefinic hydrocarbons the following method may be employed. It is suitable for analysis of samples containing from 0·2 to 100 per cent of butadiene and for the lower amounts may be regarded as a micro-method.

This apparatus[1] is based on the Diels-Alder reaction involving the addition of a conjugated olefine to maleic anhydride with the formation of a six-membered ring containing one double bond.[2] The analyser was developed by the Universal Oil Products Company and E. H. Sargent & Co.,[3] in accordance with the specifications of the former company.

The apparatus Fig. 15 (XVIII^3) consists of a 500-ml. gas sampler, a drying-tube, a U.S. Bureau of Standards type burette and compensator assembly, the absorption-pipette containing maleic anhydride and an expansion-bulb, together with the necessary levelling-bulbs for passage of the gas sample. Connexions between the burette, absorption pipette and the expansion-bulb are made with spherical interchangeable ground joints firmly held with special clamps providing considerable flexibility for connexions and thus reducing materially possibility for breakage of glassware. Mercury is used as the confining liquid except in the case of the gas sampler where a saturated sodium sulphate solution is used. The absorption-pipette consists of a U-tube filled with glass beads of 5-mm. diameter to present a large surface for the absorption of butadiene by the maleic anhydride. The U-tube is ring sealed into a cylindrical glass jacket which is provided with an inverted well for the insertion of a cartridge heater of sufficient heating capacity to raise the water in the cylindrical jacket to the boiling temperature in order that the maleic anhydride in the U-tube may be kept molten. Steam generated in the water jacket is condensed by a 4-in. reflux condenser. The apparatus is also provided with a control panel containing a switch controlling the heater and another switch and neon light for actuating the compensator which indicates the attainment of atmospheric pressure in the system. All glass parts are mounted on adjustable supports on a steel frame.

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[1] Made by Arthur H. Thomas Co., Philadelphia, U.S.A.

[2] *Biochem. Z.*, 1934, *269*, 177; *Ber.*, 1902, *35*, 3915; *ibid.*, 1907, *40*, 2033. *See also ibid.*, 1908, 2233, 1914, 1659.

[3] Chicago, Illinois, U.S.A.

SECTION 2: MANOMETRIC METHODS

Many biological and also some chemical reactions can be studied by the manometric method, which was originally devised by Barcroft and Haldane in 1902 and modified by Warburg.[1] In general the manometers used are of three main types. The first is the constant-pressure type where a graduated tube containing liquid is attached to the apparatus: the liquid in this tube is adjusted so as to maintain the pressure constant and the volume change is read off from the tube. The Winterstein micro-respirometer is an example.

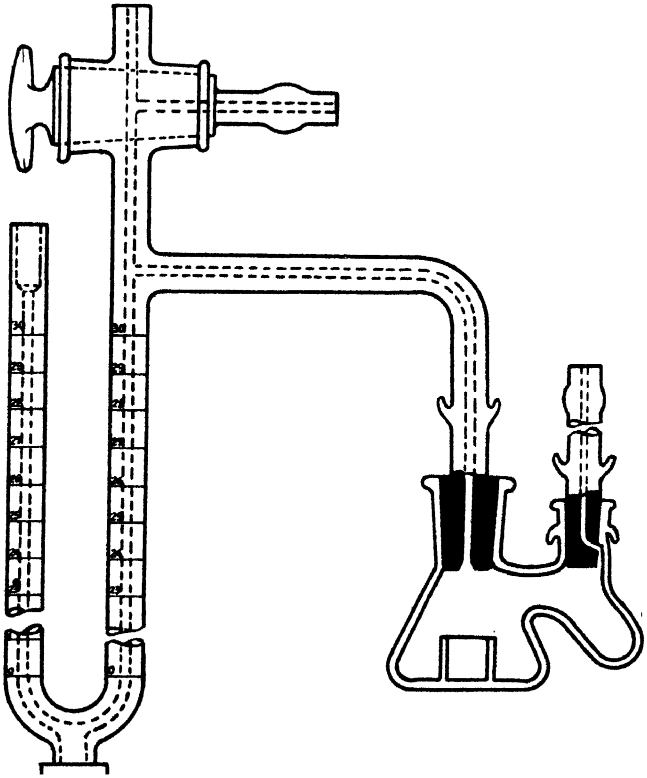

FIG. 16 (XVIII[3])
The Warburg apparatus

The second type is a constant-volume instrument which has a U-tube manometer open on one side to the air. This is the type originally devised by Barcroft and Haldane but now generally called the Warburg type.

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[1] *Über den Stoffwechsee der Tumoren*, Springer, Berlin, 1926; English translation, F. Dickson, Constable, London, 1930.

In the third, or differential type, both pressure and volume undergo change. Here instead of the end of the manometer being open to the air it is attached to a second vessel similar to the first so as to eliminate errors due to small temperature changes. This model is called the Barcroft type. The Warburg Manometer is the one most generally used.

Constant-Volume Respirometer

Warburg's apparatus is shown in Fig. 16 (XVIII³). The U-tube of pyrex glass has an external diameter of 8 mm.; the bore should be uniform and 1 sq. mm. in cross-section in order to give the necessary sensitivity. The arms are graduated to 30 cm. in mm. At the bend of the manometer a rubber reservoir with a screw clamp allows the adjustment of the manometric liquid. One end of the U-tube is open to the air and the other has a three-way tap on it and also a horizontal side-tube bent down and with a standard taper ground joint by which reaction vessels can be attached. The three-way tap allows of connexion to the air or the introduction of any desired gases.

The U-tube is attached to a board or metal sheet and has a metal slide by which it can be attached to a shaker. When the reaction vessel is placed in the thermostat the U-tube rests on the outside of the thermostat and the same mechanism agitates the liquid in the thermostat and gives a to-and-fro motion to the manometer.

Before making a reading the indicating fluid is always brought to a fixed point—usually the 150-mm. mark—on the right arm by adjusting the thumbscrew on the reservoir. The reading is then made on the left-hand arm and the difference in pressure between the inside of the reaction vessel and atmospheric pressure is obtained by subtracting 150 mm. from the reading.

Dixon[1] and Perkins[2] deduce the following equation for the volume of gas absorbed or evolved.

$$x = h\left[\frac{V_g\frac{273}{T} + V_f(\alpha)}{P_0}\right]$$

where x = cu. mm. of gas at standard temperature and pressure.
h = reading of manometer (change in height in manometric graduations).
V_g = free volume of gas in the vessel and manometer to the level of manometric fluid (total volume of apparatus less volume of sample, liquids, and detachable supports placed in the vessel).
T = absolute temperature of the water-bath surrounding the vessel.
V_f = volume of all liquids in the vessel in which the measured gas might dissolve.

[1] *Manometric Methods*, C.U. Press, 1943.

[2] *Ind. Eng. Chem. Anal.*, 1943, *15*, 61.

α = solubility of the gas being measured in the vessel liquid at temperature T (*see* Bunsen's solubility table).

P_0 = normal pressure in terms of manometric fluid (for Brodie's solution, 10,000 mm.). Brodie's solution may be prepared as follows : sodium chloride, 23 grams ; sodium tauroglycocholate, 5 grams ; water to 500 ml. (10,000 mm. of this solution are approximately equivalent to 760 mm. of mercury).

The quantity in the square bracket is constant for a given vessel with a given gas provided that the temperature and the liquid volume remain the same. Under these circumstances the equation becomes $x = k.h$.

The value of k is not affected by the presence of a second gas such as nitrogen, but is of course different for two gases such as oxygen and carbon dioxide which have different solubilities.

T and V_f are given by the conditions of the experiment and α is obtained from tables of physical constants. P_0 can be calculated from a density determination of the solution and V_g is obtained by subtracting the value of V_f from the total volume ; this is determined by filling with mercury to the 150 mm. and weighing the mercury.

Barcroft Differential Respirometer

This instrument[1] is next in popularity to Warburg's. A diagram is shown in Fig. 17 (XVIII[3]) of Dixon and Elliot's modification.[2]

The pyrex U-tube has an internal diameter of 0·5 mm. and an external diameter of 6–7 mm. The graduations on each arm run from 0 to 200 mm. The two special flasks should match each other in volume to 0·1 ml. if compensation is to be satisfactory.

The theory for this apparatus is worked out in Dixon's book and he gives a simplified formula which may be used provided that certain conditions are fulfilled, particularly that the area of cross-section of the U-tube shall not exceed 0·5 sq. mm. Then

$$x = h\left(\text{Cos}\,\theta + \frac{AP_0}{2V_g'}\right)\left(\frac{V_g\frac{273}{T} + V_f\alpha}{P_0} + \frac{A}{2}\cdot\frac{273}{T}\right)$$

where x = cu. mm. of gas evolved in reaction vessel (right flask).

h = manometer reading.

A = area of manometer bore in sq. mm.

V_g' = vol. of gas space in (left) compensating flask, including manometer tubes to the level of manometric fluid, normally kept at 100 mm. mark.

V_g = volume of gas space in (right) reaction flask.

T = absolute temperature of thermostat.

α = solubility of gas being measured in vessel liquid at temperature T.

V = volume of all liquids in the vessel in which the measured gas might dissolve.

P = normal pressure in terms of manometric fluid.

θ = inclination to vertical of manometer tube.

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[1] *J. Physiol.*, 1908, *37*, 12.

[2] *Biochem. J.*, 1930, *24*, 820.

Calibration. This can be carried out from the formula in the manner already described or by the method of Munzer and Neumann.[1] One of the flasks is connected to a tube which bears a 1-mm. pipette with levelling-tube containing mercury, a manometer containing paraffin and a tap.

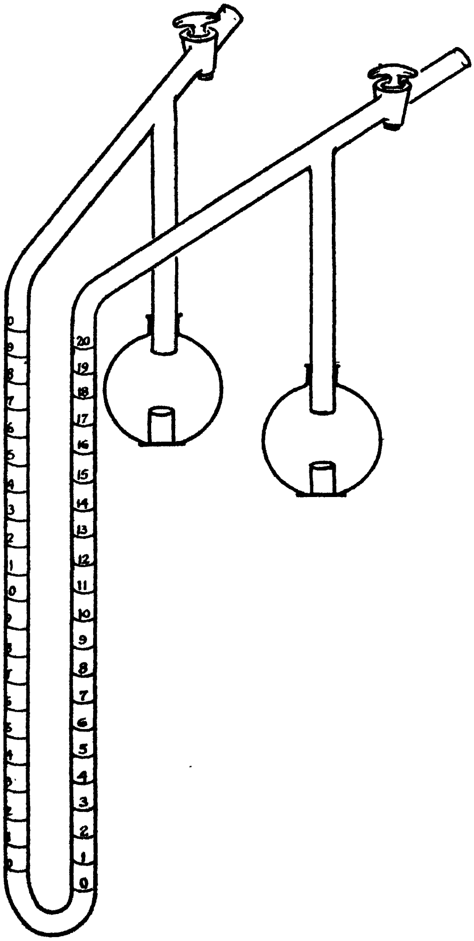

FIG. 17 (XVIII^{3})
Barcroft differential manometer with flasks

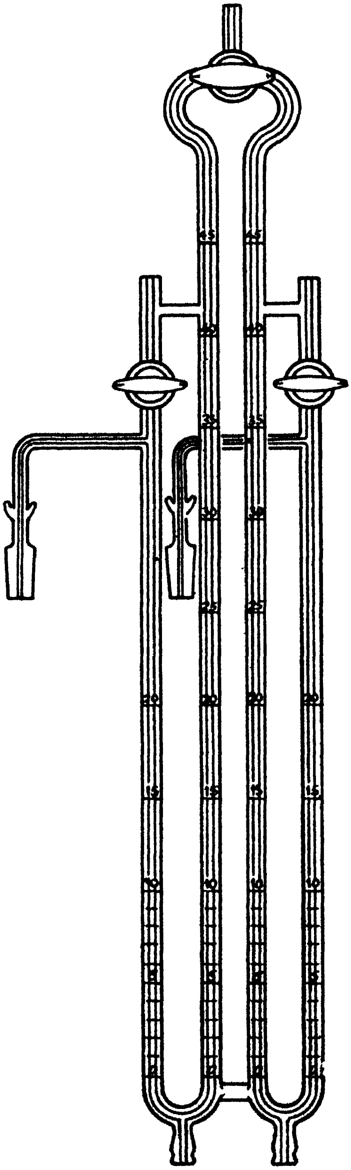

FIG. 18 (XVIII^{3})
Constant-volume differential manometer

The flasks and the pipette are placed in the thermostat with the three taps open and the reaction flask (2) containing an amount of water equal to that which would be used in an experiment. The air in the pipette is mixed with that in flask 2 by closing the tap 3 and raising and lowering the levelling-tube.

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[1] *Biochem. Z.*, 1917, *81*, 319.

After 15 minutes close taps 1 and 3 and take readings of the Barcroft manometer and of the pipette (in cubic millimetres). Lower the levelling-tube to withdraw some air from flask 2 to the pipette, close tap 2, adjust the levelling-tube so that the paraffin manometer reading is the same as before and again read the Barcroft manometer and the pipette. So we obtain the volume x' of air withdrawn measured at atmospheric pressure and at the temperature of the water-bath and we also have the corresponding reading of the Barcroft manometer, say h'. Now correct x' to dry gas at N.T.P. obtaining x and get k from $\frac{x}{h'}$.

Summerson Constant-Volume Differential Manometer

This apparatus, described by Summerson,[1] is shown in Fig. 18 (XVIII[3]). It consists essentially of two Warburg manometers mounted together as one instrument and having the open end of their U-tubes connected by a T-tap. Its great advantage lies in its adaptibility. With the T-tap turned so as to join both sides to the air it becomes two Warburg manometers or one manometer and a thermobarometer. With the T-tap turned through 180° it becomes a constant-volume differential manometer.

Readings are made along the two inner arms which are graduated from 0 to 450 mm. The manometer liquid is maintained at the calibration marks on the outer tubes by the usual device of a pressure screw on the rubber fluid reservoir.

Fenn Differential Volumeter

This instrument is more widely used in America than in Europe. It is similar to that devised by Thunberg,[2] but since it has been largely used by Fenn,[3] his name is generally connected with it. It consists of two vessels connected by a horizontal capillary. In this is a drop of oil stained with Sudan III dye to act as an index. If the Barcroft differential instrument had its manometer tilted up until it became horizontal and $\cos\theta$ became zero; putting $d = \frac{h}{2}$ when d is the distance in millimetres through which the oil moves in the capillary, we obtain the expression

$$x = d\left[\left(\frac{V_g\frac{273}{T} + V'_f\alpha}{V'_g\frac{273}{T} + V'_f\alpha} + 1\right)\frac{P - p}{P_0}\cdot\frac{273}{T}\right]$$

in which the symbols have the same meaning as before. The capillary is made of precision bore pyrex tubing of 0·3 sq. mm. cross-section and the graduations run from 0 to 150 mm.

The experimental flask has two side-arms 90° apart for the transfer of contents and a stop-cock for the introduction of different gas mixtures.

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[1] *J. Biol. Chem.*, 1939, *131*, 579.

[2] *Zentr. Physiol.*, 1905, *19*, 308.

[3] *Am. J. Physiol.*, 1927, *80*, 327.

The volume of each flask is about 15 ml., and results with this apparatus appear to be about equal in accuracy to that obtained with other forms.

Methods of measuring Respiration. Two methods are in use, the simpler one in which the oxygen taken up is measured directly and the other in which it is obtained by indirect calculation. In the direct method the carbon dioxide produced is taken up by alkali and so has no effect on the manometer which records only the oxygen used up. The objection to it is that it cannot be used with solutions containing bicarbonate, as the *p*H quickly becomes too high owing to the absorption of carbon dioxide by the alkali. In the case of animal tissues this makes the conditions unphysiological owing to the absence of bicarbonate.

To overcome this objection, in the indirect method the carbon dioxide is not absorbed and the oxygen uptake and carbon dioxide output are obtained indirectly, either by making use of the great difference in solubility between oxygen and carbon dioxide or by the introduction of reagents into the vessel at various stages of the experiment. For details the reader is advised to consult Dixon's book (*v.s.*). A differential mercury manometer was used by Eversole and Hanson [1] to measure the lowering of the vapour pressure of sulphur dioxide by potassium iodide. The manometer was made of 6-mm. pyrex tubing and was approximately 2 metres high. It was connected with two thin-walled pyrex bulbs of 40 ml. capacity as shown schematically in Fig. 19 (XVIII^3). A weighed portion of pure potassium iodide was placed in one bulb through the side-arm, the other bulb being empty. The two bulbs were then connected to a hyvac pump at the side-arms, and the whole system evacuated and heated to remove adsorbed gases and air occluded by the mercury. After flushing the system twice with sulphur dioxide vapour, sulphur dioxide was distilled simultaneously into the chilled bulbs. The side-tubes were then sealed, and the bulbs set in a constant-temperature water-bath. When uniformity of temperature was

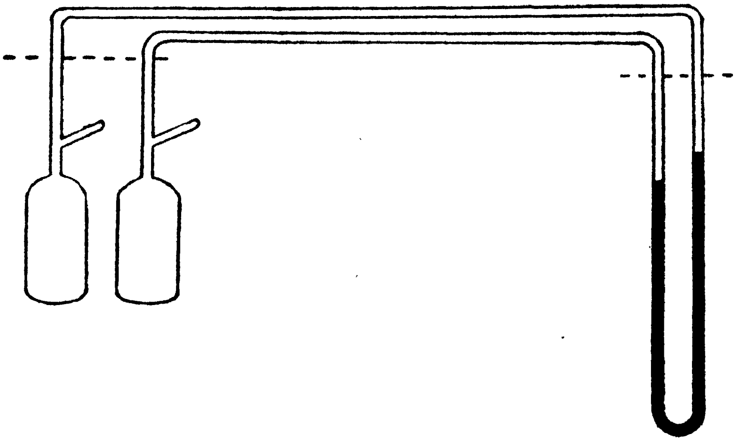

FIG. 19 (XVIII^3)
The apparatus of Eversole and Hanson using a differential mercury manometer

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[1] *J. Phys. Chem.*, **1943**, *47*, 1.

reached, the mercury levels in the manometer were read using a travelling-microscope. With concentrated solutions, when there was a greater difference than 15 cm. in the readings, a cathetometer was used. The bulb containing the solution was sealed above the side-tube for subsequent determination of the sulphur dioxide present.

In the microrespirometer of Heatley, Berenblum, and Chain [1] a micro-manometric method is used to measure very minute quantities of gases. The amount of gas which can be estimated is approximately 200 times smaller than can be estimated in the Warburg apparatus. The instrument is capable of measuring intake and output of the order of 1μl. hr. The apparatus can be assembled at one temperature and used at a widely different one; it can be filled with any gas mixture, and two or more separate fluids contained in it can be mixed at any desired time during an experiment. No special care is required according to the authors, and the experiment takes slightly longer than in the case of the Warburg or Bancroft apparatus. During the course of an experiment six readings can, with practice, be taken in five minutes. It can also be used under sterile conditions which is important in certain types of biological work. The principle of the apparatus is shown diagrammatically in Fig. 20 (XVIII[3]). In the actual instrument the two reservoirs, consisting of 85-ml. bottles suspended horizontally, are attached to opposite sides of an endless chain passing round a system of pulleys and sprockets. A control wheel fixed to one of the latter enables the pressure in the system to be varied. For filling the cups with any desired gas mixture, a main tube having a number of side-tubes is connected to the gas source; a separate bubbler, containing water and immersed in the thermostat, is interposed between this manifold and each respiration vessel, partly to moisten the gas, and partly to enable the rate of passage of gas in each individual case to be checked. It is important that the gas should be as nearly saturated as possible before entering the vessel, as otherwise evaporation of the droplets may occur, with alteration in the volume of the fluid and thus of the vessel constants.

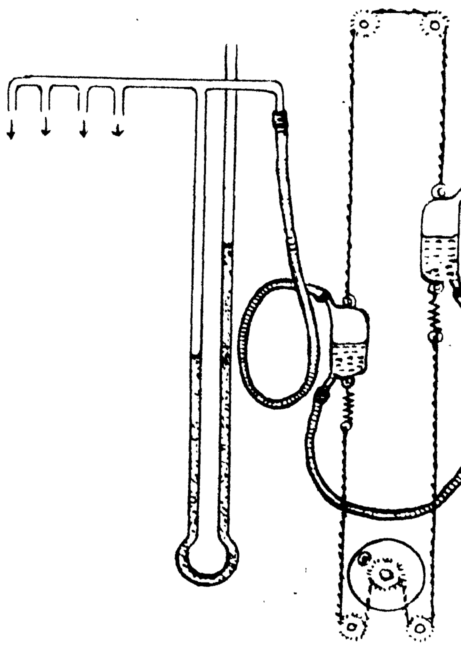

FIG. 20 (XVIII[3])
The microrespirometer apparatus of Heatley, Berenblum, and Chain

It was found that when dry oxygen was passed through the respiration chambers via the bubblers, for 10 minutes at 37° at the rate of 5–10 ml./min., only about 0·5 µl. of fluid was lost from a drop of 12 µl. of distilled water. The evaporation can be reduced still further by inserting a plug of damp cotton-wool in the rubber tube connecting the case to the bubbler. A thermobarometer is required, as in the Warburg technique, to compensate for any changes in thermostat temperature or barometric pressure. Since the volume of the vessel used as thermobarometer is immaterial, a simple bulb connected to a manometer of capillary tubing serves the purpose.

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[1] *Biochem. J.*, 1939, *33*, 53.

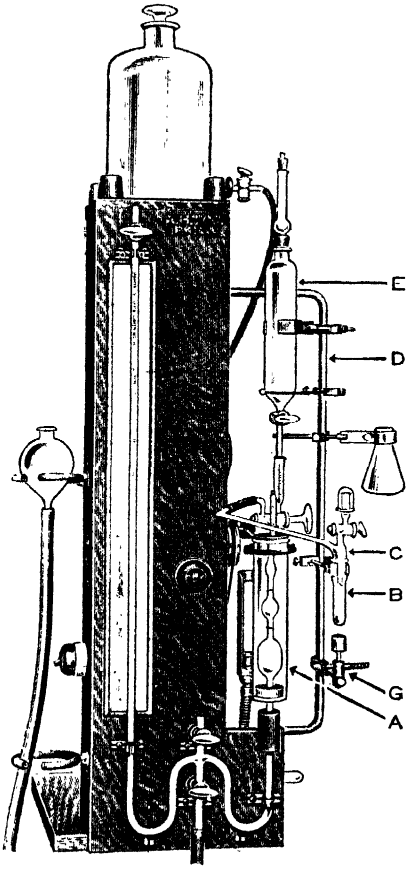

FIG. 21 (XVIII[3])
Apparatus for the determination of combustion gases by a manometric method.

Estimation of Carbon Monoxide in Blood by Manometric Methods

This estimation has been described by van Slyke and Neill.[1] The oxygen and carbon dioxide, carbon monoxide and nitrogen are liberated by shaking in vacuo with acid ferrocyanide. The oxygen and carbon dioxide are then absorbed with alkaline hyposulphite. In a more accurate method Sendroy and Liu [2] transfer the gases to a Hempel pipette containing alkaline pyrogallol, and the oxygen and carbon dioxide are absorbed in a van Slyke–Neill chamber; the carbon monoxide is absorbed by cuprous chloride. A modified method has been described by Roughton.[3] It can be used in Barcroft differential manometers as well as in the van Slyke–Neill manometers. The principle of the method is to fix the oxygen and carbon dioxide with alkaline glycinate-hyposulphite mixture and at the same time to evolve the nitrogen into the gas phase. The only remaining gas in solution is then carbon monoxide, which is subsequently liberated by shaking with neutral ferricyanide solution. In the van Slyke–Neill apparatus the method gives accurate results (analysis can be carried out on a 2-ml. sample of blood), and the technique is simpler than is the former apparatus since no special gas-absorbing reagents are required.

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[1] *J. Biol. Chem.*, 1924, *61*, 523.

[2] *Ibid.*, 1930, *89*, 133.

[3] *Ibid.*, 1941, *137*, 617.

In the Barcroft apparatus the technique is equally convenient, but the results are not quite so accurate.[1]

Manometric Combustion Apparatus

For the determination of carbon compounds manometric methods have been devised for the determination of the combustion gases. In the method of van Slyke and Folch [2] the complete and rapid oxidation of the sample is brought about by the action of fuming sulphuric, phosphoric, chromic, and iodic acids. This 'wet'-combustion method gives results comparable with the dry-combustion method in accuracy. The carbon dioxide gas is measured in the apparatus [3] shown in Fig. 21 (XVIII[3]). It consists of a digestion tube, a gas-absorption tube, and a manometer.

Combustions can be made on samples containing from 0·3 to 3·5 mg. of carbon. Complete oxidation is effected in 1 to 3 minutes, reducing the time of a routine analysis to approximately 20 minutes. The presence of nitrogen, sulphur, halogen, &c., does not affect the result.

The assembly consists of the van Slyke–Neill blood gas apparatus with combustion-tube B attached to absorption-chamber A by connecting-tube C. The absorption-chamber is calibrated at 10 ml. as well as at the usual 0·5-, 2·0-, and 50-ml. marks. Accessories conveniently attached to support D are separatory funnel E for adding alkaline hydrazine solution, micro-burner G, and Erlenmeyer flask, with necessary spring-grip clamps and holders.

Estimation of Active Hydrogen

This estimation may be made directly by measurement of methane evolved. A better technique involving an indirect method is described below. The method was devised by Soltys [4] for the determination of active hydrogen atoms and groups of molecules which react with Grignard reagent. When the Grignard reagent adds to the reacting molecule and no methane or other gaseous hydrocarbon is evolved, the method may still be employed. The unused Grignard reagent is caused to react with aniline and the volume of hydrogen generated measured. A simple direct volumetric method for the determination of active hydrogen has also been developed.[5] A manometer method has also been devised.

The original method of Soltys is based on the precedure of Tschugaeff and Zerewitinoff.[6] A short description of the A.H.T. Soltys active hydrogen apparatus will be given.[7] The method has been standardized as to mechanical features and arrangement, with accessories for preparing Grignard reagent, and Benedetti-Pischler drying-block. Accuracies within approximately 1 per cent are possible but depend upon the structure of the compound. Determinations can be made with milligram samples.

The apparatus (Fig. 22 (XVIII[3])) consists of a reaction vessel A (methane generator), gas burette (manometer) B, air-driven shaking apparatus C, and thermometer, mounted on a support, and necessary spring-grip clamps, burette meniscus reader, train for drying and regulating the pressure of nitrogen, and accessory equipment. This consists of: Train for drying nitrogen gas, consisting of drying tube M and gas washing bottle N; and Friedrich gas pressure valve P for maintaining constant nitrogen pressure. Grignard reagent preparation apparatus R, on support S with Coors porcelain base and necessary spring-grip clamps. Benedetti-Pichler drying-block T, improved form, modified to accommodate a measuring-pipette and reaction flask F. With micro-burner and thermometer. Wash bottle X, 250-ml. capacity, with fused-in white label, with saliva trap and movable capillary tip.

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[1] *Loc. cit.*

[2] *J. Biol. Chem.*, 1940, *136*, 509.

[3] The model is made by Arthur H. Thomas Co., U.S.A.

[4] *Mikrochemie*, 1936, *20*, 107.

[5] Feaschentrager, *Z. physiol. Chem.*, 1923, *146*, 219; Roth and Daw, *Quantitative Organic Microanalysis of Pregl.*, pp. 156–66, Blakiston's Son & Co., Philadelphia, 1937.

[6] See ref. 4; also Niederl and Niederl, *Organic Qualitative Micro Analysis*, 2nd ed., 1943, J. Willy & Son, New York.

[7] Apparatus made by A. H. Thomas Co., Philadelphia, U.S.A.

The reaction vessel F has an interchangeable ground joint and coil springs for attaching reaction flask, and an interchangeable stopper with coil springs at side opening of storage chamber. The measuring tube of the reaction vessel, for introduction of Grignard reagent, has automatic zero adjustment and is graduated from 0 to 2 ml. The side-tube with open top for introducing aniline is graduated from 0 to 1 ml. Both tubes are in 0·02-ml. divisions. The stop-cocks have special locking devices to prevent leakage under pressure during shaking. The gas burette with manometer is graduated from 0 to 7 ml. in 0·02 ml. Similar graduation marks on burette and manometer are at the same level. Either pressure or vacuum can be used to operate the air-driven piston drive shaking device which can be started and stopped by a flick of the finger on the fly-wheel. The apparatus for preparation of Grignard reagent is mounted on a corrosion-resistant stand with Coors porcelain base. Capacity of the flask is 200 ml. The Benedetti-Pichler drying-block has a recess in the top to fit the reaction

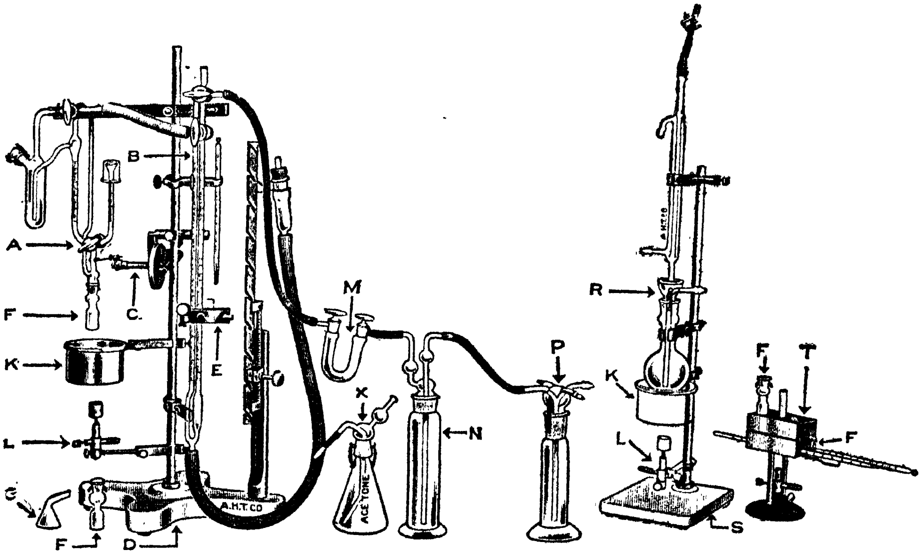

FIG. 22 (XVIII³)
The Thomas active hydrogen apparatus

flask and a horizontal chamber to fit pipettes required for the Soltys-technique.

Manometric Liquids (*see* Vol. I, p. 560). It should be mentioned that, for example, R. Fuess-Berlin supplied a special manometric liquid mixture of density 2·0 which increases the range of manometers. This liquid does not mix with water and is therefore not affected with water-vapour measurements. The form of the meniscus is unobjectionable, the congelation takes place at − 11°. Further, it is noteworthy that by admixture of certain substances it is possible to remove the surface tension (meniscus) of water in a manometer.

Alcohol has a lower specific weight than water and gives greater deviations with the same overpressure, but its coefficients of thermal expansion and evaporation are greater. Concentrated alcohol absorbs water from the air and therefore changes its density. In order to make the liquid more visible, admixtures of dyes are used. Only very few are suitable, as they separate and stick to the glass walls of the manometer tube. R. Fuess-Berlin recommends[1] Rhodamin aniline dye. First of all, a concentrated solution of Rhodamin is prepared in alcohol, after settling down, a small quantity of the clear alcoholic solution is added to the manometric liquid.

In the case of paraffin oil or Xylol it should be noted that the thermal expansion coefficient is 5 times that of water. Dilute sulphuric acid (specific weight = 1·05), has certain advantages. With average air humidity very little water evaporates, while with high humidity no vapour is absorbed. Readings of nearly all liquid manometers must, however, be reduced to a reference temperature.

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[1] According to J. Grunow in Kleinschmidt's *Handbuch.*

SECTION 3: DIELECTRIC CONSTANT METHOD

(*See* Vol. II, Chap. XIII)

The dielectric constants of the gases do not differ very much from one another; but so sensitive are the means available for their examination that the determination of the dielectric gas constant forms a suitable basis for analysis in a number of cases. They can be used for small amounts of gas and come under the heading of micro-methods. There are two methods in general use. In one the gas to be analysed is placed in a small cell which occupies the space between the plates of a condenser. This is coupled to an impedance so that together they form an oscillating circuit. According to the dielectric constant of the gas, so the natural frequency of the circuit alters. It is usually measured by a comparison with a suitable wave-meter oscillator.

In the second method, the tuned circuit is caused to oscillate by means of a suitable thermionic valve circuit. The frequency thus generated is caused to mix with that produced by a second calibrated oscillator, and the latter is adjusted until a beat note of constant pitch is produced. In all cases the instruments are calibrated by placing in them gases of known composition.[1] In the method of Groves and Sugden [2] the dielectric constant of the vapour at a known temperature and pressure is measured by a reasonance method using the circuit shown in Fig. 23 (XVIII³).

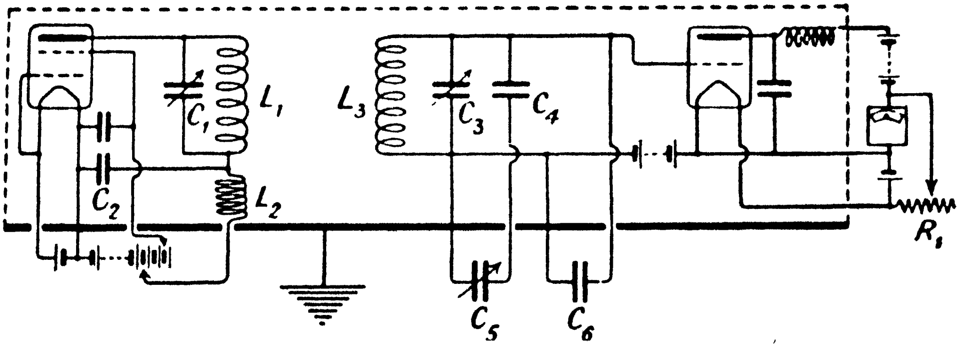

FIG. 23 (XVIII³)

Circuit for the measurement by a resonance method of the dielectric constant of a vapour

The oscillator is of the Dynatron type, using a Mullard P.M. 12 screened-grid valve. This type of oscillator has been found by Groves and Sugden to give greater stability of frequency and amplitude than a quartz crystal oscillator. The high-frequency radiating circuit consists of the inductance L_1 and the capacity C_1; the high-frequency current was restricted to the anode-filament circuit by means of the choke and blocking condenser L_2 and C_2.

Hartridge, *J. Sci. Inst.*, 1939, *16*, 324.

[2] *J. Chem. Soc.*, 1934, 1094.

The coil L_1 and the pick-up coil L_3 were wound on specially constructed formers consisting of two ebonite rings joined at the edges by ebonite rods. This arrangement gives the minimum amount of dielectric in the field of the coil, and, by reducing energy absorption, makes the resonance curve sharper. The frequency used is approximately 1,000 KC.; and the field strength such as to give a resonance potential across L_3 of about 9 volts with a distance of 25 cm. between the parallel coils L_1 and L_3.

The resonance coil is tuned by the system of condensers C_3, C_4, C_5, and C_6. C_3 is an inexpensive variable condenser for rough tuning, and is maintained at a fixed capacity during a series of measurements. C_6 represents the capacity of the cell containing the vapour; the small change in capacity of C_6 when vapour is admitted to the cell or removed from it is measured by the combination $C_4 - C_5$ of the two condensers in series. C_4 is small, of the order of 10 $\mu\mu$F, while C_5 is a Sullivan standard variable condenser of maximum capacity 1,200 $\mu\mu$F. It is clear that for a given state of resonance, a small change in capacity of C_6 (itself of the order 100 $\mu\mu$F) will require a large change in C_5 to bring the circuit back to the same state of resonance. On this principle depends the accurate measurement of the small changes occurring in C_6 as a result of the introduction of vapours and gases. In order to obtain a high sensitivity on the galvanometer, conditions are adjusted to give a very sharp resonance curve. This is done by making a series of experiments with the receiving coil at varying distances from the oscillator for various values of grid bias. From a set of such measurements, the sharpest curve is obtained when the coils are separated by 25 cm., and the grid bias is –9 volts.

In making measurements, the galvanometer is used as a null instrument. The circuit is tuned by C_3 until a point half way up the resonance curve is reached, where under the above conditions of grid bias, &c., the sensitivity of the apparatus is such that 1 per cent change in capacity of C_6 effects a 10 per cent change in anode current. (The anode current at its peak is of the order of 120–30 micro-amps.)

A typical measurement is made in the following manner.[1] The cell C_6 is evacuated, and the anode current adjusted by C_3 to the appropriate point on the resonance curve, maintaining a large reading on C_5. The resistance R_1 is adjusted until the bulk of the anode current is balanced out, leaving a suitable small reading as constant reference point. Vapour or gas is then introduced into C_6, producing a small increase in capacity; this is compensated by reducing the value of C_5 until the galvanometer records the same value for the anode current as it did before the admission of the gas. If C_5 and C_5' be the readings of the measured condenser before and after the admission of gas, then it is easily shown ΔC_6—the change in capacity of C_6 is given by

$$\Delta C_6 = C_4^2(C_5 - C_5')/[C_5C_5' + C_4(C_5' + C_5' + C_4^2]$$

Hence $\varepsilon - 1$ is given by

$$\varepsilon - 1 = \frac{\Delta C_6}{C_6} = \frac{C_4^2}{C_6} \cdot \frac{C_5 - C_5'}{C_5C_5' + C_4(C_5 + C_5') + C_4^2} \quad . \quad . \quad (1)$$

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[1] *Loc. cit.*

It should be noted that C_6 in equation (1) is the replacable capacity of the cell, and does not include the stray capacities of leads, &c.; the term C_4^2 in the denominator is very small and can be neglected.

The cell consists of two stainless steel cylinders fixed concentrically with a gap of about 1 mm. It is sealed inside a large bulb immersed in an electrically heated oil-bath. Leads are taken from the inner and outer cylinder to mercury cups on the top of the vessel. In use the outer cylinder and the iron vessel containing the oil-bath are earthed.

Calibration of Cell. It will be seen from equation (1) that the dielectric constant of the cell contents can be deduced from an apparatus constant C_4^2/C_6, the initial and final reading of the measuring condenser C_5, and an approximate knowledge of C_4. The latter need not be known with great accuracy since the term in the denominator of (1) involving C_4 is small compared with the product C_5C_5'. The cell is therefore calibrated by making observations with gases of known dielectric constant.

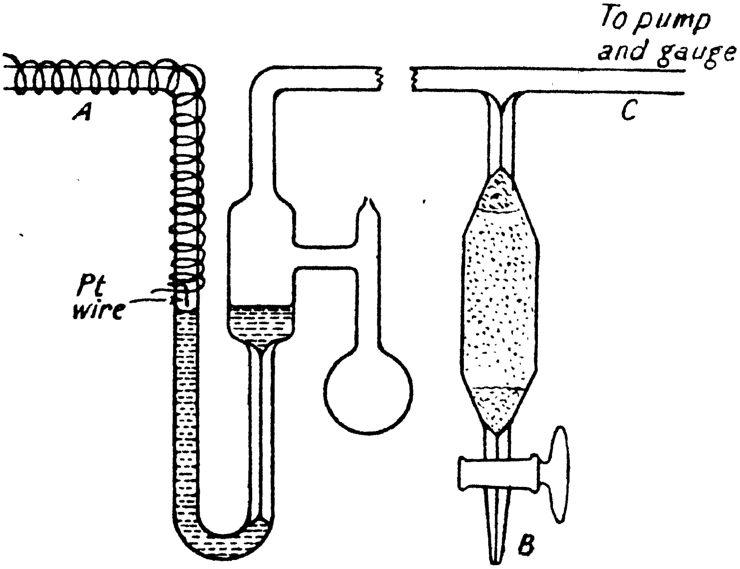

FIG. 24 (XVIII^a)
Modified Mills apparatus for the admission of vapour to the cell

From measurements of Bryan and Sanders,[1] Stuart,[2] and Zahn [3] the mean polarization of air was taken as 4·368 ml. and that of carbon dioxide as 7·317 ml. It being assumed that the polarization of these gases does not change with temperature and that the gas laws hold, the dielectric constant of the gas at a known temperature and pressure may be calculated by the relation

$$\varepsilon - 1 = Pp \times 4{\cdot}810 \times 10^{-5}/T \quad . \quad . \quad . \quad (2)$$

where P is the molecular polarization, p, the pressure in millimetres of mercury and T the absolute temperature.[4]

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[1] *Phys. Rev.*, 1928, *32*, 202.
[2] *Z. Physik.*, 1928, *47*, 457.
[3] *Phys. Rev.*, 1926, *27*, 455.
[4] Groves and Sugden, *loc. cit.*

Control of Vapour or Gas.—The most convenient method of admitting vapour to the cell is a slight modification of the apparatus of Miles [1] shown in Fig. 24 (XVIII^3).[2]

The tube A leading to the cell in the oil-bath is heated electrically with nichrome wire lagged with asbestos. A suitable quantity of liquid is introduced into the bend of the U-tube and cooled by a freezing mixture. The cell is evacuated through tube C, and a little dry air admitted through the leak B. Regular ebullition in the left-hand limb is facilitated by the platinum wire sealed into the heated limb. Air is swept out of the cell by admitting vapour and pumping it out several times, leaving a few millimetres pressure of vapour in the cell. By careful manipulation of B, any desired pressure of vapour can be introduced into the cell or rapidly removed by opening the connexion to the pump. The pressure recorded on the gauge is corrected for any difference of level of the liquid in the arms of the U-tube.

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[1] *Ibid.*, 1929, *34*, 964.

[2] *J. Chem. Soc.*, 1934, *2*, 1096.

CHAPTER XIX[3]

ANALYSIS OF MIXTURES

SECTION I: MULTIPLE PHASES

(*See* the Phase Rule, Vol. I, p. 171)

FOUR-Component Diagrams. Certain problems may arise in physico-chemical work which involve the study of four-component systems. Van 't Hoff used this method to determine the exact temperature at which the beds of the Stassfurt salt-deposits, embracing the chlorides and sulphates of magnesium and potassium, were laid down. Quaternary systems have important applications in the investigation of compounds formed in the setting of Portland cement and by the action of sulphate waters on concrete. Some workers have studied the direct evaporation of sea-water bittern by the investigation of such a system, with a view to the possible exploitation of the potash content of sea water. Furthermore, isothermal diagrams of such systems have been used to determine the best conditions for obtaining different salts from solution by crystallization.

The best exposition of the graphical representation of such systems has been given by Schreinemaker,[1] by whose method it is always possible to determine exactly the composition of the solid phase in equilibrium with any given solution in any one of four ternary systems which comprise a quaternary system.

Any quaternary system is constructed from four ternary systems, a study of which ought to be incorporated in an investigation of the higher system. These ternary systems may be, as previously shown, graphically represented by means of triangles, but quaternary systems necessitate the use of a regular tetrahedron for their graphical representation. The vertices of the figure correspond to the four components, the edges to mixtures of the two components represented by the vertices which the edge in question joins; the faces each represent one of the four ternary systems which arise from the components, and quaternary phases are represented by points within the figure. Mixtures with a constant ratio of two of the components lie on planes through the edges joining the other two; when the ratio of three of the components is constant, the corresponding mixtures lie on a line through the fourth vertex.

For illustrative purposes, and to simplify the determination of quantitative relationships, a projection of the pyramid on to one of its faces is employed. This method has been expounded by Schreinemaker[2] in his investigation of the equilibria of the system water (W), alcohol (A), lithium sulphate (Li), and ammonium sulphate (A*m*).

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[1] *Z. physik. Chem.*, 1908, *65*, 553; 1910, *71*, 109.

[2] *Loc. cit.*

He gives the following interpretation of the various diagrams shown below. Fig. 1 (XIX^3) illustrates the equilibrium of the system at 6·5°.

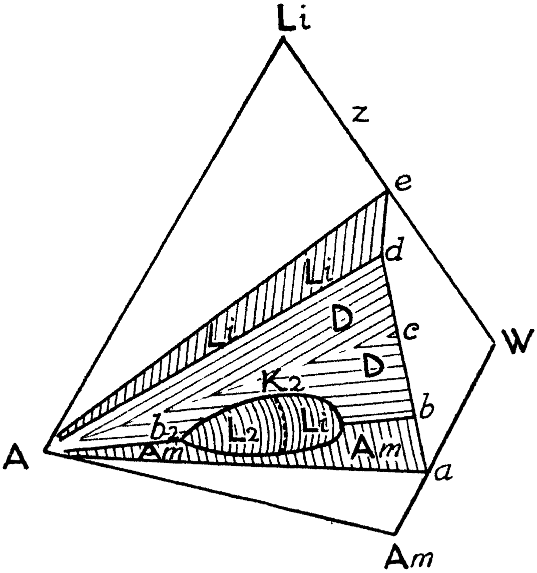

FIG. 1 (XIX^3)
Equilibrium in the system—water, ethyl alcohol, lithium sulphate, and ammonium sulphate at 6·5°

The points *a* and *e* give the solubilities of A*m* and Li in water. At 6·5° no formation of liquid layers occurs in the ternary system W, A*m*, A, so the solubility of ammonium sulphate in water-alcohol mixtures is represented by the line *a*A.

The equilibrium water, lithium sulphate, ammonium sulphate, is shown on the side W, Li, A*m*; *ab* is the saturation curve of ammonium sulphate.

Solutions saturated with respect to solid $(NH_4)_2SO_4$ are shown by the surface A*m* which is bounded by Ab_2, K_1, b_1, *ba*A. The saturation surface of the double salt is denoted by D.

At 6·5° division into two liquid layers can take place in none of the ternary systems, but this happens in the quaternary system. These equilibria are represented by the surfaces L_1 and L_2 which are called binodal surfaces.

The equilibrium was also developed at 30° and is shown in Fig. 2 (XIX^3). The saturation surface A*m*, which at 6·5° was all one, is now divided into two portions. This division occurred when the

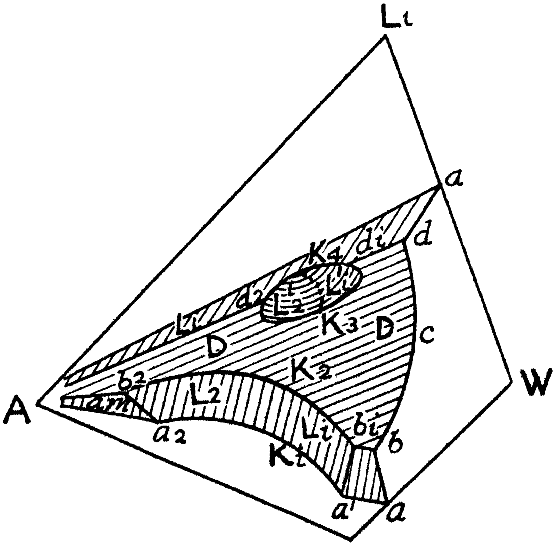

FIG. 2 (XIX^3)
Equilibrium in the system—water, ethyl alcohol, lithium sulphate, and ammonium sulphate at 30°

binodal surface reached the ternary boundary AWA*m*. The binodal surface L_1L_2 also cuts two surfaces of saturation, namely DLi and Li, so that it also gives a series of two liquid equilibria. The curve A*c* represents the solubility of the double salt in alcohol-water mixtures. Fig. 3 (XIX³) shows the equilibrium at 50°. Graphical deduction of quantative relationship is carried out as follows :

The system is represented by the tetrahedron with vertices A, W, Li, and A*m*. In the space diagram, the quantities of the four components which a point inside the tetrahedron represents may be found in the following manner. To find the quantity of alcohol a straight line is drawn through the point parallel to one of the three sides A, A*m*, A, Li, or A, W. The quantity of alcohol is represented by the length of this line measured from the point itself to the intersection of the straight line with the plane W, Li, A*m*. The lengths of the various parallel lines are the same. In a similar manner can be found the quantities of the three other components.

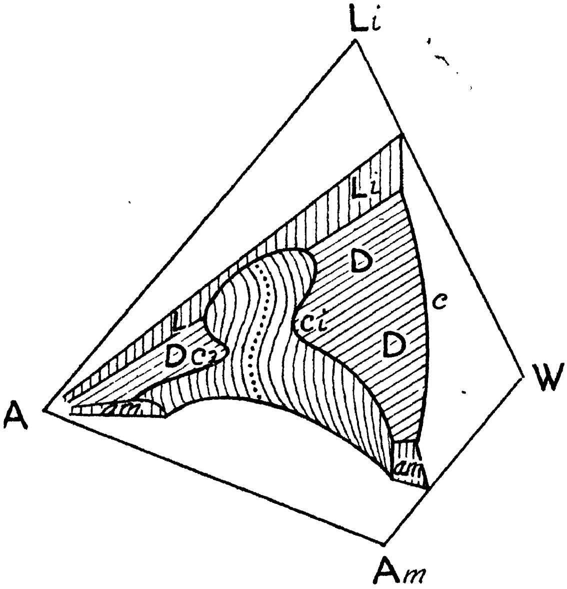

FIG. 3 (XIX³)

Equilibrium in the system—water, ethyl alcohol, lithium sulphate, and ammonium sulphate at 50°

Let there be present x per cent alcohol, y per cent $(NH_4)_2SO_4$, z per cent Li_2SO_4 and therefore $100 - (x + y + z) =$ per cent of water.

The point is taken as origin and W, A, W, A*m*, and W, Li as X, Y, and Z axes. As co-ordinates of a point the perpendicular lines are not taken but lines parallel to the axes. The point is now projected on the plane A, W, A*m* in such a manner that the line of projection is parallel to the side W, Li. The x and y, i.e. alcohol and ammonium sulphate, remain unaltered. Similarly, the point may be projected on the plane (or face) A, W, Li, so that the projection line is parallel to the axis W, A*m*, and x and z will remain constant, or on the plane W, Li, A*m*, with y and z remaining unaltered. Two of these three projections are enough to determine all the desired quantities. If therefore the projections on the plane A, W, A*m*, and that on the plane A, W, Li be taken, the first gives the alcohol and ammonium sulphate and the second the alcohol and lithium sulphate.

In plotting the projection of a tetrahedron the relative proportions of only three of its components are represented, that of the fourth being in a direction at right angles to the paper.

Reciprocal Salt Pairs

The four-component system referred to above comprised water and three salts with a common ion. If the restriction of a common ion be removed quaternary systems may arise from a mixture of two salts with water. This is due to the possibility of double decomposition between the salts.

If the reaction represented by the interaction of $NH_4Cl + NaNO_3$ be considered, the two pairs of salts $NH_4Cl + NaNO_3$ and $NaCl + NH_4NO_3$ may be regarded as reciprocal salt pairs, since one pair is formed from the other double decomposition. Two reciprocal salt pairs do not in themselves comprise a quaternary system, since only three components are embodied. The fourth may be expressed in terms of the other three. Thus from the equation

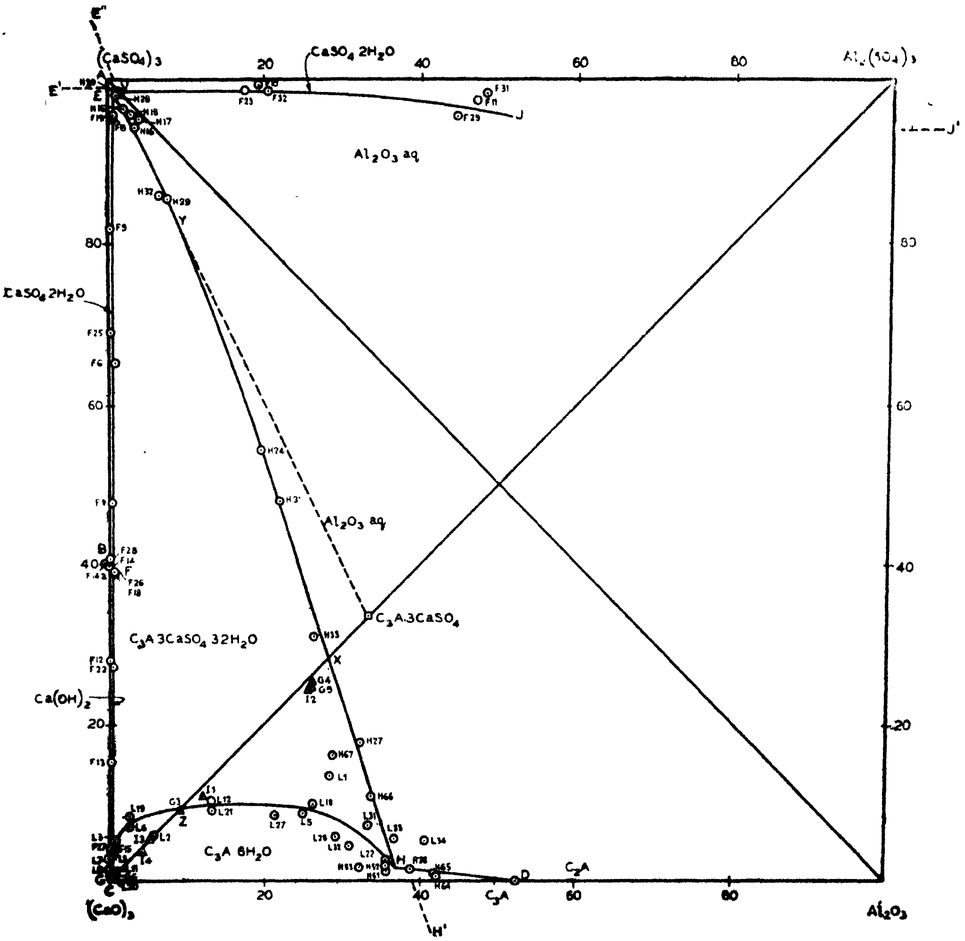

FIG. 4 (XIX[3])
Quaternary system—CaO—Al_2O_3—$CaSO_4$—H_2O (Jones)

$$A + B = C + D$$

D may be written as A + B − C. Hence the number of components is three, any three of the four salts. The addition of a solvent (water) raises the system to quaternary status.

Such a system is best represented graphically by the method of Lowenherz [1] who chose a regular tetrahedral pyramid to represent the four components. The four corners of the base of the pyramid represent the four salts, adjacent corners carrying salts with common ions, and thus salt pairs are represented at opposite corners of the square. The apex of the pyramid represents the pure solvent. When this method of representation is employed illustratively the basal orthogonal projection of the pyramid is the medium adopted. Such a projection is shown in Fig. 4 (XIX[3]) taken from the paper of Jones [2] on the quaternary system $CaO—Al_2O_3—CaSO_4—H_2O$ at 25° (4). The projection of the edges of the pyramid for two axes are at right angles, which give rise to four quadrants each representing one of the four constituent ternary systems. The exposition by Jones of the figure is as follows:

The system was considered as being formed by the reciprocal salt pairs $Ca(OH)_2$ and $Al_2(SO_4)_3$ aq., and Al_2O_3 aq. and $CaSO_4$ aq. The following reaction occurs:

$$(Ca(OH)_2)_3 + Al_2(SO_4)_3 \text{ aq.} = Al_2O_3 \text{ aq.} + (CaSO_4)_3 \text{ aq.}$$

It is essential in this method of representation that the composition of mixtures be expressed in molecular percentages, and also that the four salts shall be related by the equation

$$1 \text{ mol. } AB + 1 \text{ mol. } CD = 1 \text{ mol. } AD + 1 \text{ mol. } BC$$

The boundary curves and invariant points shown are as follows:

(*a*) Ternary system $H_2O—(CaO)_3—Al_2O_3$

$H_2O—D = Al_2O_3$ aq.
$D = Al_2O_3$ aq.—$(CaO)_3.Al_2O_3.6H_2O$
$DC = (CaO)_3.Al_2O_3.6H_2O$
$C =$ Solubility of crystalline $Ca(OH)_2$ in water

(*b*) Ternary system $H_2O—(CaSO_4)_3—CaO$

$CB = Ca(OH)_2$ (crystalline)
$B =$ crystalline $Ca(OH)_2—CaSO_4.2H_2O$
$BA = CaSO_4.2H_2O$
$A =$ solubility of $CaSO_4.2H_2O$ in water

(*c*) Ternary system $H_2O—(CaSO_4)_3—Al_2(SO_4)_3$

$Al = CaSO_4.2H_2O$

(*d*) Ternary system $H_2O—(CaSO_4)_3—Al_2O_3$

This system was not investigated, as it is not of direct interest in cement chemistry.

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[1] *Z. physik. Chem.*, 1894, *13*, 459.
[2] *Trans. Faraday Soc.*, 1939, XXXV, 12, 224, p. 1484.

(*e*) Quaternary system

(i) Boundary curves

JE = $CaSO_4.2H_2O—Al_2O_3$ aq.
EH = Al_2O_3 aq.—$(CaO)_3 Al_2O_3 3CaSO_4 32H_2O$
EF = $CaSO_4 2H_2O—(CaO)_3 Al_2O_3 3CaSO_4.32H_2O$
BF = $CaSO_4 2H_2O—Ca(OH)_2$
FG = $Ca(OH)_2—(CaO)_3 Al_2O_3 3CaSO_4 32H_2O$
GC = $Ca(OH)_2—(CaO)_3 Al_2O_3 6H_2O$
GH = $(CaO)_3 Al_2O_3 6H_2O—(CaO)_3 Al_2O_3 3CaSO_4 32H_2O$
HD = $(CaO)_3 Al_2O_3 6H_2O—Al_2O_3$ aq.

(ii) Invariant points

E = $CaSO_4 2H_2O—Al_2O_3$ aq.—$(CaO)_3 Al_2O_3 3CaSO_4 32H_2O$
F = $CaSO_4 2H_2O—Ca(OH)_2—(CaO)_3 Al_2O_3 3CaSO_4 32H_2O$
G = $Ca(OH)_2—(CaO)_3 Al_2O_3 6H_2O—(CaO)_3 Al_2O_3 3CaSO_4 32H_2O$
H = $(CaO)_3 Al_2O_3 3CaSO_4 32H_2O—(CaO)_3 Al_2O_3 6H_2O—Al_2O_3$ aq.

Janecke's Method. A method of representation devised by Janecke[1] has the advantage over Lowenherz's that the composition of the solution is expressed in terms of ions, or acidic and basic radicles instead of salts.

Janecke employed a rectangular column (Fig. 5 (XIX^3)) on a square base for complete representation of the isothermal equilibria of reciprocal salt-pairs on the three-dimensional scale. By this means, the systems of aqueous solutions arising from the salt-pair P_1Q_1 and P_2Q_2, with its reciprocal pair P_1Q_2 and P_2Q_1, can be represented by the following

$$xP_1 ; \ (1-x)P_2 ; \ yQ_1 ; \ (1-y)Q_2 ; \ zH_2O^\circ$$

where x ; $(1-x)$; y ; $(1-y)$ are the number of gram-molecules of the ions dissolved in z gram-molecules of water. The four corners of the base again represent the pure salts, salts with a common ion being placed at adjacent corners.

The sides AB and CD of the square will represent solutions containing different proportions of P_1 and P_2. If these sides are divided in the ratio of x to $(1-x)$, giving the points L and M the line LM will represent quaternary solutions in which the ratio of P_1 to P_2 is as x to $(1-x)$. Similarly the line NR can be plotted to give the composition of all quaternary solutions in which the ratio of Q_1 to Q_2 is as y to $(1-y)$. The point of intersection of these lines, O, will now represent the solution of composition xP_1 ; $(1-x)\,P_2$; yQ ; $(1-y)Q_2$, all dissolved in a given amount of water. This amount of water can be represented by erecting a perpendicular at O and marking off a length corresponding to z gram-molecules. This point in space now gives the solution of the composition

$$xP_1 ; \ (1-x)P_2 ; \ yQ_1 ; \ (1-y)Q_2 ; \ zH_2O$$

In practice the plane quadrangular diagram is employed. The amounts of the various salts are represented graphically, but the amount of water is given by numericals only.

The following figure is a projection isothermal (for 25°) according to the methods of Janecke for the system of salt-pairs (Na, K—NO_3, Cl) and solvent water.

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[1] *Z. physik. Chem.*, 1908, *51*, 132; 1911, *71*, 1.

This system Fig. 6 (XIX^3) has useful applications in the manufacture of saltpetre from sodium nitrate and potassium chloride, and has been studied by Reinders.[1]

The four corners A, B, C, D, represent respectively the four salts $NaNO_3$; KCl; KNO_3; and NaCl. Isohydrores, or lines of equal water content, have been omitted.

The diagram is broken up by the solubility curves into areas some of which are contingent and some not. Thus the area KNO_3, which represents solutions saturated with respect to KNO_3, touches the area KCl along the line RT, and this line represents the solutions from which these two salts may separate together. Now the area $NaNO_3$ and KCl do not touch, so that it is impossible to prepare a solution from which these two salts will separate simultaneously. If now a solution of 50 per cent $NaNO_3$ and 50 per cent KCl, in sufficient water, be prepared it is clear from the diagram that this solution will be represented by the point X and will lie in the KNO_3 area. On evaporation, therefore, the salt KNO_3 will separate out, and the changing composition of the mixture will be represented by the line XT, travelling away from the KNO_3 corner. At T, the curve ST is encountered and co-crystallization of NaCl and KNO_3 can occur.

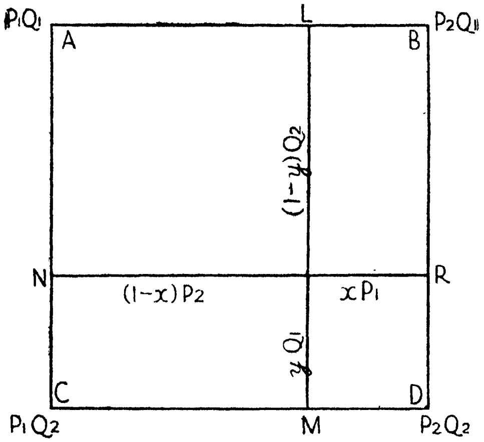

FIG. 5 (XIX^3)

Janecke's representation of the isothermal equilibrium of reciprocal salt-pairs on the three-dimensional scale

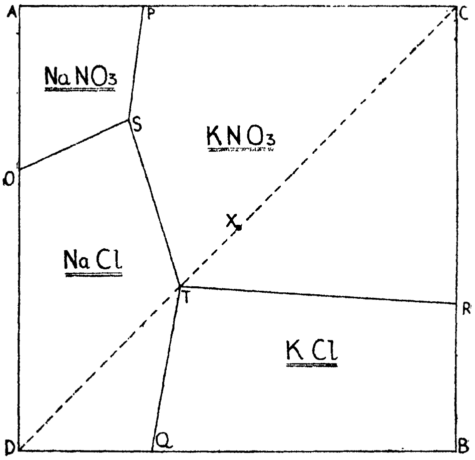

FIG. 6 (XIX^3)

Projection isothermal at 25° for the system of salt-pairs (Na, K—NO_3, Cl) and water (as solvent)

NaCl and KNO_3 are called the stable pair, and KCl and $NaNO_3$ the unstable pair at this particular temperature. The point O represents a solution which is saturated for $NaNO_3$ and NaCl. At Q, it is saturated for NaCl and KCl. Similarly at P and R the solution is in equilibrium with $NaNO_3$ and KNO_3, and KNO_3 and KCl, as the solid phases respectively.

The point S represents a solution saturated for the three solid salts $NaNO_3$, NaCl, and KNO_3. Lying as it does entirely within the triangular area ACD, all points on which represents solutions the composition of which can be expressed in terms of these three salts, the point S therefore represents a congruently saturated [1] solution, that is to say a solution from which the solid phases are continuously deposited during isothermal evaporation to dryness. On the other hand, in an incongruently saturated solution at least one of the solid phases disappears during the process of evaporation. Similary the point T represents a solution congruently saturated with respect to NaCl, KNO_3, and KCl.

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[1] *Z. anorg. Chem.*, 1915, *93*, 202.

A solution represented by a point in any one of the four areas of the figure will be in equilibrium with the solid phase appertaining to that area. If for example a point in the area APSO be taken, it will represent the composition of a solution in equilibrium with sodium nitrate as the single solid phase.

On isothermal evaporation of such a solution sodium nitrate will separate out, and the composition of the solution will change in a straight-line direction from the corner A until a point on one of the curves OS,SP is reached, when a second solid phase will begin to separate out.

Reinders investigated the above system with a view to determining the best conditions under which potassium nitrate can be prepared by the double decomposition between sodium nitrate and potassium chloride. He found that the best yield of potassium nitrate working between the temperatures 5° and 100°, is obtained by mixing 0·80 gram-molecules of sodium nitrate, 0·52 gram-molecules of potassium chloride, and 1·81 gram-molecules of water, at 100°. Solid sodium chloride (0·42 gram-molecules) is deposited, and the mother liquor is then cooled down to 50°. 0·371 gram-molecules of water is added, and 0·563 gram-molecules of potassium nitrate crystallize out. The cycle is then repeated by heating the mother liquor to 100°. During each cycle 90·8 per cent. of the potassium chloride is recovered as potassium nitrate, or from 100 grams of original solution at 100° there are obtained 46·6 grams of potassium nitrate.

Fedotieff [2] studied the reciprocal salt pair system (Na,NH^4)—(Cl,HCO_3), H_2O which arises in the Solvay ammonia-soda process for the manufacture of sodium carbonate. The process, which involves passing carbon dioxide through a solution of common salt saturated with ammonia, may be represented by the equation

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

From Fig. 7 (XIX^3), after Fedotieff, it can be seen that in this case the stable pair are $NaHCO_3$ and NH_4Cl. Therefore, on mixing NaCl and NH_4HCO_3 in saturated solution, $NaHCO_3$ is precipitated.

Fedotieff found that in the Solvay process it is more economic to work with solutions which are relatively rich in sodium chloride.

Natural Salt Deposits

The deposition of natural salts by oceanic evaporation, such as has given rise to the famous Stassfurt deposits, has been exhaustively studied by Van 't Hoff and others, who investigated the isothermal equilibria of the reciprocal salt-pair (K, Mg)—(Cl, SO_4) and allied systems. Since large numbers of double salts are formed, each with a definite temperature range, it has been found possible, on discovering the existence of certain double salts in the beds, to predict the temperature of formation to within a few degrees.

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[1] When two solid phases are deposited simultaneously from a solution, that solution is said to be congruently saturated (Meyerhoffer, *Ber.*, 1897, *30*, 1809).

[2] *Z. physik. Chem.*, 1904, *49*, 162.

Salt Pairs : Working Method

The following general description of the method best calculated to obtain one salt-pair from its reciprocal pair is due to Findlay.[1] Calling the unstable pair of salts reactants and the stable pair resultants, the following temperature cycle is employed.

To a solution called a nucleus solution equivalent quantities of the reactants are added, in such amount as to produce a solution saturated with respect to one resultant only, at the upper limit of the temperature range employed in the process. The solid resultant is separated from the mother liquor, which is cooled down to such a temperature that a quantity of the second resultant is deposited equivalent to the amount of the first resultant deposited at the upper temperature. When the second resultant is removed the mother liquor has the composition of the nucleus solution, and the cycle may be repeated. If water has to be added to adjust the solutions at any stage, it is removed at a later stage.

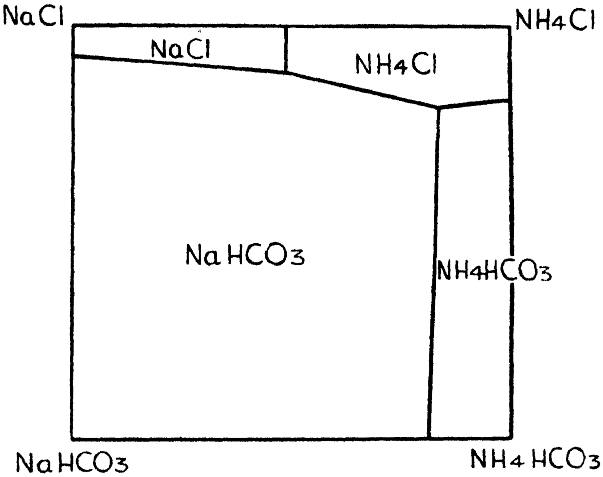

FIG. 7 (XIX³)
The system $NaCl—NH_4Cl—NaHCO_3—NH_4HCO_3$ (Fedotieff)

Multi-Component Systems

Systems of more than four components can obviously not adequately be represented even by a solid model. Van 't Hoff, in his study of the marine salts, worked with a five-component system, but graphical representation was possible since the solutions were saturated throughout with respect to one component, sodium chloride, which was therefore disregarded in constructing the isothermal diagrams. Similarly it will be possible to represent six-component systems if we assume that the solution is saturated with two salts. Such systems have not been much studied, apart from the above-mentioned work by Van 't Hoff.

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[1] *The Phase Rule and its Applications.* Longman, 7th ed., 1935.

SECTION 2: ANALYSIS OF AGGREGATES

The physical analysis of solids is considered in Chapter III, Vol. II, pages 135–48. Notes on some related tests are given here.

Electric Precipitators[1] **or Electrostatic Dust Samplers.** In these a measured volume of dust-laden air is passed through a cylindrical glass collecting-tube fitted with a central wire electrode maintained at a potential difference of up to 15,000 volts with respect to a gauze electrode wrapped round the tube. The electric field produced results in an electrostatic attraction of the particles of dust and in their being charged by the corona electric discharge, the effect of which is to drive them in a direction normal to the motion of the air along the tube. The dust particles are precipitated on the inside surface of the glass tube or upon a thin celluloid lining placed inside the tube, from which they can be washed into water or other liquid for sedimentation and evaluation as with the Impinger samples. The study of dust particles has also been made by the electron microscope.[2]

The determination of the size of small particles which are too small to be graded by means of sieves is often a matter of importance, as for example with cements, pigments, pulverized coal, cosmetics, and insecticides. Methods which have been used include suspension in a liquid and turbidity measurements, microscopic measurements of size, and elutriation with air currents. A method which is capable of giving results which are sufficiently accurate for most technical purposes and which gives the average particular size involves the use of the apparatus shown in Fig. 8 (XIX[3]).

This apparatus[3] records measurements of particles from 5×10^{-3} cm. down to 2×10^{-5} cm. The method is based on the resistance to the passage of air offered by the packed participles. The air current flows more readily through the interstices in a bed of coarse powder than through an otherwise similar bed of fine powder.

A sample of the powder of weight in grams equal to its density is packed to a known degree in the sample tube which is of precision bore and where it is retained between the porous plugs LL. Air from a small electrically driven motor pump enters at P and its pressure is regulated by the simple device shown at R. It then passes through the drier D and up through the sample S and on to the flowmeter; in this the air passes through the standardized capillary C to the outlet at O, the pressure difference on the two sides of C being measured by H, the head of liquid in the manometer M. Consideration will show that since there is a constant pressure below the sample at S, if the material is coarse, the air will get through freely and there will be a large pressure difference on the two sides of C. If the material is fine, less air gets through with a correspondingly smaller reading on the manometer. The apparatus has been standardized with powders of known particle size and a chart is provided with the aid of which and the observed height H the average particle size can be read off in microns (10^{-4} cm.).

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[1] Drinker, Thomson, and Fitchet, *J. Indust. Hyg.*, 1923, *5*, 162.

[2] Fress and Müller, *Gasmaske*, 1939, *11*, 1.

[3] Made by Fisher Scientific Co., Pittsburgh.

The Physical Testing of Cement.

Cement is a typical example of a coarse aggregate. An account is given here of the method by which a product such as Portland cement is examined.[1]

Measurement of Specific Gravity. The specific gravity of cement is conveniently determined by the liquid-displacement method using kerosene as the displacement liquid (*see* Chap. XII, Section 2, Vol. I).

Measurement of Setting Time. Two stages of setting are recorded in the laboratory—the ‘ initial set ’ and the ‘ final set ’. In the determinations of ‘ setting times ’ the cement is gauged with the required amount of water to give a paste of ‘ normal consistency ’. The paste is then filled into a cylindrical mould and the surface is smoothed off level with the top of the mould. The test mould is kept during the whole time of the test at a temperature of 58°–64° F. in an atmosphere of not less than 90 per cent relative humidity.

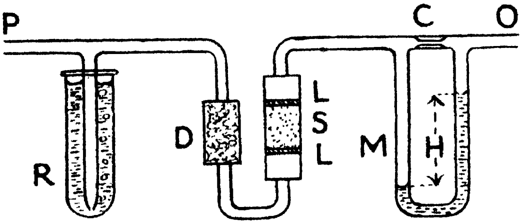

FIG. 8 (XIX[3])
Apparatus for the measurement of fine particles
(5×10^{-3} cm. to 2×10^{-5} cm.)

For the determination of initial setting time the test-block is placed under the rod of the Vicat apparatus bearing the ‘ initial setting time ’ needle. This needle is 1 mm. square in section and has a flat end. The needle is gently lowered into contact with the surface of the block and quickly released. Initial set is said to be reached when the needle by its own weight is no longer able to penetrate the test-block completely. The interval of time elapsing between adding the water and the formation of initial set is called the initial setting time.

For the determination of final set the needle used is fitted with a metal attachment hollowed out so as to leave a circular cutting edge 5 mm. in diameter, the end of the needle projecting 0·5 mm. beyond this edge. Final set is said to have taken place when this needle gently applied to the surface of the test-block makes an impression on it, but the circular edge of the attachment fails to do so. The interval of time elapsing between adding the water to the cement and the formation of final set is called the final setting time.

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[1] The authors are indebted to Dr. D. J. Ryan for the greater part of the notes on cement testing. They are also indebted to Mr. F. E. Jones of the Building Research Association, Herts, for helpful advice.

The Vicat apparatus is generally used. It consists of a frame bearing a movable rod. The needles for the determinations of setting times and a plunger for determining the normal consistency can be attached to the bottom of the movable rod. The weight of the rod plus any of the attachments is constant (300 grams).

Other Methods. (1) The Gillmore apparatus (Fig. 9 (XIX^3)) is mentioned at A.S.T.M. Designations (C77 ; C91 ; C141) and in Federal Specifications (SS–C–158 and SS–C–18lb.). The cement is considered to have acquired initial set when the test-block will bear without appreciable indentation the Gillmore needle 1/12th in. diameter loaded to weigh ¼ lb. Final set is considered to have taken place when the block will bear without appreciable indentation the Gillmore needle 1/24th in. diameter loaded to weigh 1 lb.

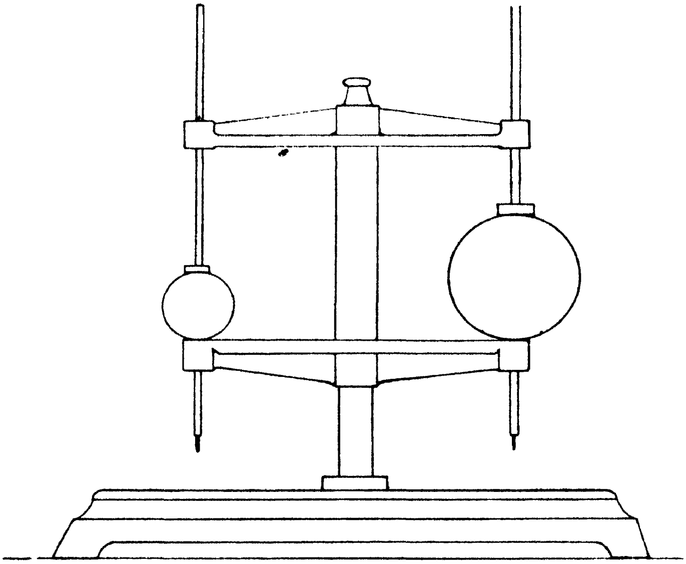

FIG. 9 (XIX^3)

The Gillmore apparatus for the measurement of '*setting*' times

(2) A self-recording device called the 'Cadograph' has been invented by the Southern Portland Cement Co. of Berrima, New South Wales. The apparatus is driven by a ¼-h.p. motor with a speed of 1,450 r.p.m. through a gearbox with a ratio of 15,000 to 1. Several samples may be tested at the same time by placing them on rotating tables which alternately rotate while the needles are at the highest point of travel. The needles which are weighted to 300 grams are lowered into the test-block at the rate of 40 mm. in 60 seconds. Attached to the needle assembly is a pen which records each penetration on a chart. Initial set is reached when the pen records 1 mm. from the base line of the chart, and final set is recorded when

the pen records 0·5 mm. from the top line of the chart. Other self-recording devices are mentioned in a paper by Davey.[1]

Measurement of Fineness. The fineness of cement for specification purposes is obtained by sifting a known weight of cement on standard sieves until the residue retained on the sieves is constant. For example, the British Standard Specification (No. 12) lays down that the maximum residue on the B.S. Sieve No. 170 shall not exceed 10 per cent when 100 grams of the cement is continually sifted by hand for 15 minutes on this sieve.

Several mechanical sieve shakers are on the market and the use of these is preferable to hand-sieving. The advantages gained by the use of these automatic shakers are as follows : (*a*) they can be used to take several sieves at a time ; (*b*) they give uniform and reproducible results ; (*c*) they simulate hand operation ; (*d*) they are quicker than hand-sieving, and (*e*) they are equipped with automatic time switches.

The inadequacy of sieves for measuring the fineness of cement has long been recognized. Several methods have been developed for measuring the particle size distribution and the specific surface (sq. cm. per gram) of cement. These will now be treated under the following heads :

(A) Photoelectric Sedimentation Methods.
(B) Pipette and Other Sedimentation Methods.
(C) Air Elutriation Methods.
(D) Air Permeability Method.

(A) 1. The Wagner Turbidimetric Method (Fig. 10 (XIX[3])). The Wagner turbidimeter consists essentially of a source of light of constant intensity, a photoelectric cell, a suspension chamber, and a mechanism for raising or lowering the photocell to permit examination of different depths in the suspension. The apparatus is mounted in a case, and includes the following features :

(*a*) *Source of Light.* The source of light is obtained from a 3- to 6-candle-power lamp operated by a 6-volts torage battery. A parabolic reflector is mounted behind the lamp and is focused to throw a beam of approximately parallel light through the suspension or sedimentation chamber, which contains a suspension of cement in kerosene. The intensity of the light is regulated by means of two rheostats of 6 and 30 ohms respectively.

(*b*) *Water Cell.* A water cell is placed in the path of the beam to absorb the larger part of the radiant heat of the beam. This cell is filled with distilled water.

(*c*) *Retarding Filter.* This enables the light intensity to be retarded over the area of that portion of the cell exposed to light during an experiment.

(*d*) *Suspension Chamber.* The sedimentation tank is constructed of plate glass cemented together to form a rectangular tank. The inside dimensions of the tank are 2 in. by 1½ in. by 8 in. in height, and the 2 in. faces of the tank are placed normal to the beam of light.

(*e*) *Photoelectric cell.* The intensity of the light which passes through the suspension chamber is measured by a Weston photronic cell and a microammeter, the microammeter readings being directly proportional to the light intensity, and thus serve as a measure of the turbidity of the suspension.

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[1] *J. Sci. Inst.*, **1933**, ***10***, **148**.

(*f*) The source of light, water cell, photoelectric cell, and retarding filter are mounted on a shelf which may be raised or lowered so as to permit examination of the suspension at any depth in the suspension chamber.

The Wagner turbidimeter depends for its action upon an application of Stokes' law to the settling time of the cement particles when suspended in kerosene, to which a few drops of oleic acid have been added. From a series of microammeter readings observed at the proper depths and time-intervals the particle size distribution from 60 microns down to 7·5 microns can be determined. Readings giving this distribution are obtained in about 10 minutes.

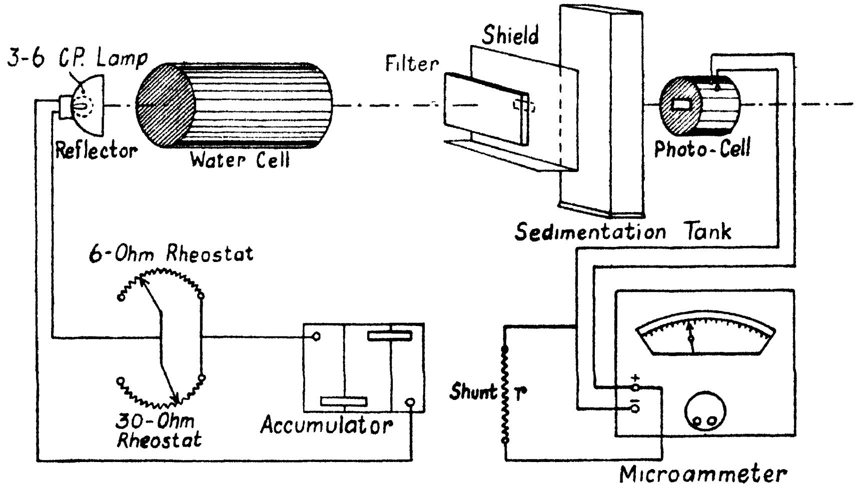

FIG. 10 (XIX[3])
The Wagner turbidimeter

The specific surface is calculated from the following equation:

$$S = \frac{38r\,(2 - \log_e I_{60})}{1{\cdot}5 + 0{\cdot}75\, I_{7\cdot5} + \log_e I_{10} + \log_e I_{15} \ldots . \log_e I_{55} - 11{\cdot}5 \log_e I_{60}}$$

where S = specific surface of the sample in square centimetres per gram, r = corrected per cent by weight passing the No. 325 sieve, and $I_{7\cdot5}$, I_{10}, $I_{15} \ldots I_{60}$ = microammeter readings in microamperes which correspond to the particle diameters 7·5, 10, 15 . . . 60 microns. The constant factor 38 applies only to a material having the specific gravity of Portland cement (3·15).

Specific Surface from One Reading. The specific surface from the first turbidity reading I_{60} may be calculated by using the following equation:

$$S = c(2 - \log_e I_{60})$$

where S = specific surface of the sample
I_{60} = microammeter reading corresponding to particle diameter of 60 microns
and c = transmittancy constant

The transmittancy constant may be evaluated by substituting in the equation known values of S and $2-\log_e I_{60}$, as determined from a complete turbidimeter test. The constant c is an average of several determinations. A schematic description of the Wagner turbidimeter is given in Fig. 10 (XIX^3). For a complete description of the apparatus and the mathematical derivation of the formulae involved reference should be made to the original paper.[1]

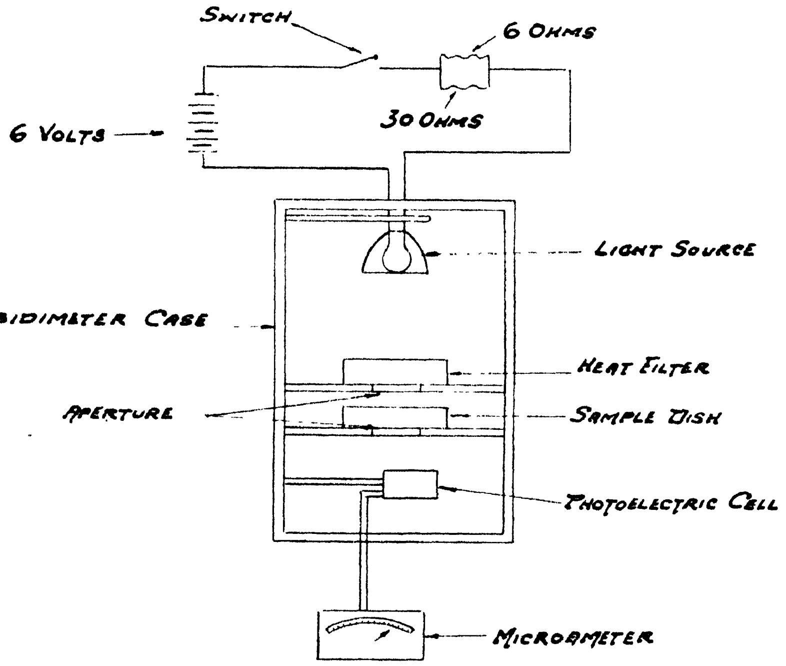

FIG. 11 (XIX^3)
The Klein turbidimeter

(A) 2. **The Klein Turbidimeter.** This instrument Fig. 11 (XIX^3) devised by Klein [2] consists essentially of the following parts:

(*a*) An adjustable source of light at the top to give a vertical beam of light;

(*b*) A heat filter consisting of a glass bottom dish containing 30 grams of clear castor oil;

(*c*) A photocell upon which falls the light that passes through the heat filter and suspension;

(*d*) a microammeter for measuring the output of the photocell; the range of the microammeter is 0–50 microamperes;

(*e*) a 6-volt storage battery.

The specific surface of a cement can be determined in one operation as follows:

With only the heat-filter in position the intensity of the light beam is adjusted to give a full scale reading on the microammeter. A 0·25 gram portion of the cement which has passed through a No. 100 sieve is added to 50 grams of castor oil in a beaker. Dispersion is accomplished by shaking and stirring with a spatula. 25 grams of clear castor oil is weighed into a sample dish and put in position in the turbidimeter. The reading I_0 is taken. The dish is now replaced by one containing 25·08 grams of the suspension and the reading I_1 is recorded. The specific surface is calculated from the equation

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[1] Wagner, *A.S.T.M. Proceedings*, 1933, *33*, Part II, 553.

[2] *A.S.T.M.*, 1934, *34*, Part II, 303.

$$S = \frac{0{\cdot}5\,(\log_e I_0 - \log_e I_1)}{K}$$

where S = specific surface in square centimetres per gram,
and K = the 'opacity factor'

The opacity factor K may be determined by a single turbidimeter test on a sample fractionated between the No. 200 and No. 325 sieves. Assuming the particles to be spherical and to have an average diameter of 0·00585 cm. the specific surface S is given by:

$$S = \frac{6}{0{\cdot}00585d}$$

where d is the specific gravity of the cement. The value of K can also be determined from the equation

$$K = (4{\cdot}035d - 10{\cdot}3)10^{-4}$$

where d = specific gravity of the cement. When the factor K has been determined for a given cement a simple chart can be prepared giving specific surface directly in terms of the microammeter readings.

B. Pipette and Other Sedimentation Methods

(B) 1. Andreason Pipette Method.[1] The Andreason pipette (Fig. 12 (XIX³)) is a vessel graduated from 0 to 20 cm. in 1-cm. divisions, with a ground-in pipette of 10-ml. capacity. The pipette is fitted with a two-way stop-cock for filling pipette and running off the sample. About 3 per cent of cement by weight is dispersed in a suitable liquid in the apparatus. The liquid most widely used is absolute alcohol, to which is added a little calcium chloride. Samples of the suspension are withdrawn at a fixed depth at selected intervals. The amount of material in these samples is estimated by evaporation in small silver dishes which are heated to 125–170° C. An application of Stokes' law permits of the calculation of the maximum size particles present in each fraction. By means of graphical methods the specific surface of the cement can be determined from its particle-size analysis. Von Gronov [2] has shown that the specific surface O of a mixture of various mineral particles, each size being of percentage p with a specific gravity s for a cubical shape of the particles:

$$O = \Sigma \frac{6}{s.d_m}.\frac{P}{100}$$

This surface can be expressed graphically as a quadrant surface

$$O = \frac{r2.\pi}{4}$$

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[1] *Zement*, 1930, 725, 19, 698.

[2] *Cement and Lime*, 1938, 55.

(B) 2. Shweyer Pipette Method. By means of the Shweyer pipette (Fig. 13 (XIX^3)) a rapid analysis of the size distribution of cement particles can be performed. The weight distribution is determined by direct weighing of the residue from a pipetted sample. A 1–2 per cent suspension of cement in water containing sodium metasilicate is used in the pipette. At exact times samples are withdrawn. Gooch crucibles or glass filters are used for collecting the samples. The crucibles are dried at a temperature not exceeding 140°.

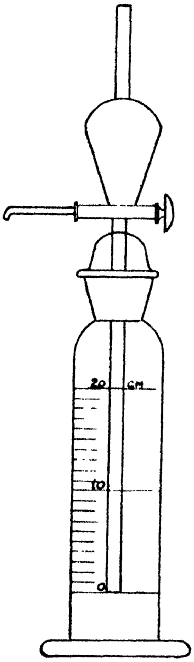

FIG. 12 (XIX^3)
The Andreason pipette

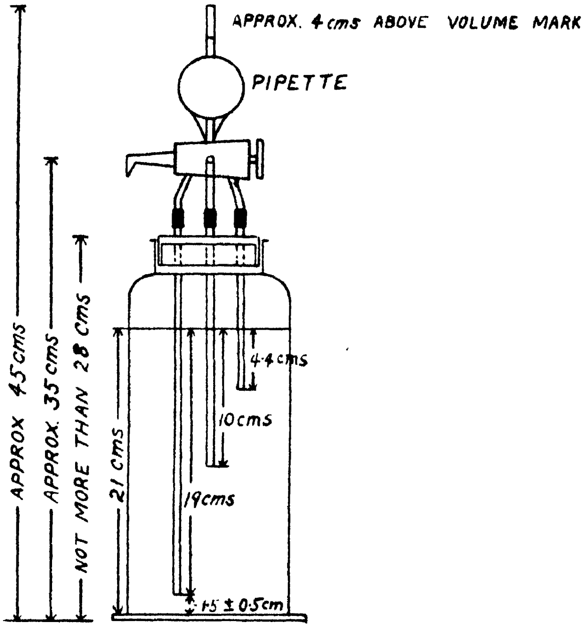

FIG. 13 (XIX^3)
The Shweyer pipette

The measurement of the concentration of particles remaining in suspension is obtained by the formula

$$G_c = \frac{100\,V_c w}{V_p W} = Kw$$

where V_c = volume of suspension at the start in cubic centimetres
w = weight of dried material in grams in a pipetted sample of V_p c.c.
W = dry weight of sample in grams at the start

The constant K for convenience of computation may be made equal to 1000 by varying the weight of the sample W, according to the calibrated volumes of the pipette and cylinder.

The size of the particles remaining in suspension after T minutes from the start of test is given by the following form of Stokes' law:

$$d = \sqrt{\frac{307 \times n \times h}{(D_s - D_l) \times T}} \text{ microns}$$

where d = equivalent spherical diameter
n = viscosity in centipoises
h = height of fall in centimetres
and D_s and D_l are the densities of solid and liquid respectively in grams per cubic centimetre.

(B) 3. **The Apparatus**[1] (Fig. 14 (XIX³)) permits the use of a suspending medium of high viscosity. The method is simple. It consists essentially of measuring the changes in pressure exerted by the suspension as the suspended material settles out. From the pressure changes the weight of material separated out is given by the expression

$$\Delta P = \frac{W_p}{A}\left(1 - \frac{d}{s}\right)$$

where W_p = weight of material that has settled out
A = cross-sectional area of the settling-tube
s = density of suspended solid
d = density of suspending medium

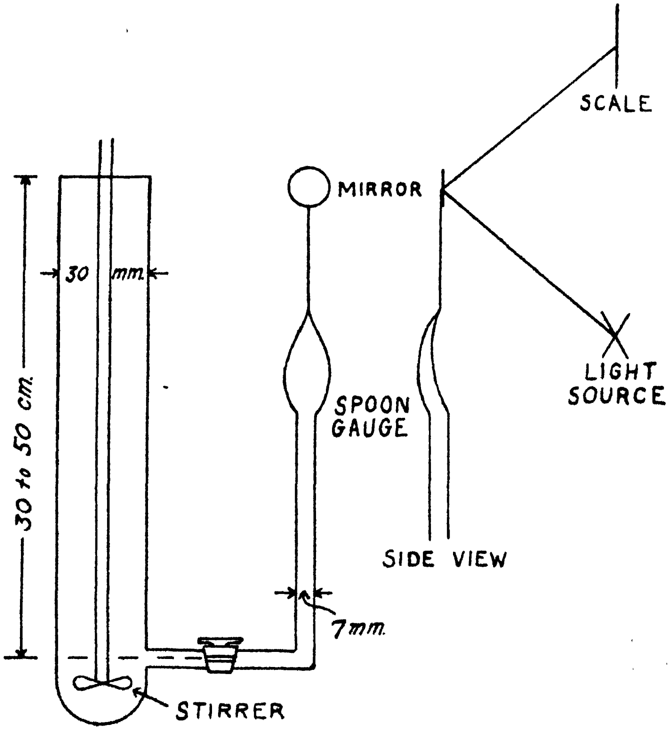

FIG. 14 (XIX³)
Apparatus for the measurement of the changes in pressure exerted by a suspension as the suspended material settles out

The settling-tube is large enough to permit the introduction of a stirring device. The spoon gauge is made from an elongated thin bulb flattened on one side. The gauge is sensitive to a pressure difference of a few millimetres of mercury. A pointer is attached to the gauge and an optical arrangement projects the pointer movement on a scale. The deflections of the pointer are converted to pressure changes by calibration of the gauge. This is done by immersing cylinders of known volumes in the liquid in the settling-tube. The increases in height of the liquid are converted to pressure increases, and these are plotted against corresponding pointer deflections. In use the apparatus is filled with the liquid to a mark. The stop-cock is closed and a weighed amount of cement is stirred in until the suspension is uniform. When stirring is stopped the stop-cock is opened and readings of the pointer deflections on the scale are taken at regular intervals.

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[1] Developed by the Pure Oil Co., U.S.A.

C. Air Elutriation Methods

In air elutriators or ‘ flourmeters ’ a weighed amount of cement is placed into a chamber or long vertical column up which flows air at a constant rate. The finer particles are taken over the top and the coarser particles which remain inside the chamber fall to the bottom when the motor-blower is stopped. The residue is weighed and the ‘ flour ’ lost obtained by difference.

The air velocity is controlled by adjusting a stop-cock so as to give the correct pressure as shown by a manometer. The maximum-size particles carried over is calculated from Stokes’ law. In practice, flourmeters are generally employed to standardize an arbitrary flour content of a cement. Various flourmeters are in general use.

The Mayntz-Peterson flourmeter consists of a tapering glass funnel, about 4 ft. high and 5-in. maximum diameter mounted vertically on a wooden stand. A calibrated flowmeter and a three-way stop-cock are mounted on the stand. The bottom end of the funnel is connected to the flowmeter. The other end of the flowmeter is similarly connected to the vertical limb of the three-way stop-cock, the lower horizontal limb of which is connected to the blower. The third limb is provided with a stop-cock which serves as a pressure release.

The Roller Particle Size Analyser.[1] The apparatus consists essentially of a U-shaped pyrex vessel for holding the sample of cement, oscillation connexions for the latter, a series of settling-chambers of different diameters, a collector for the fractions, and a gooseneck connector. The apparatus is equipped with a calibrated flowmeter and a constant-pressure motor-driven pump.

The U-shaped vessel oscillates about 200 times per minute by the action of a leather-tipper hammer mounted on a rotating shaft. The U-container is fitted to the ends of the settling-chamber. By means of the apparatus the particle size distribution of cement or any dry powder below the 200-mesh sieve can be determined. The analysis is accomplished by means of a carefully regulated current of air. A common series of fractions obtained is 0–5, 5–10, 10–20, 20–40, 40–80 microns. The different size fractions that are obtained can be examined microscopically for the purpose of checking and calibrating the instrument.

(D) Air-Permeability Method

Lea and Nurse [2] have devised an air-permeability method for the measurement of the surface area of cements. The apparatus affords a ready means of comparing the specific surfaces of powdered materials. The specific surface values obtained by this method are at variance with the results obtained by the Wagner turbidimeter. The two methods are, however, based on different assumptions and each method is essentially a comparative one.

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[1] Roller, *J. Amer. Cer. Soc.*, 1937, *20*, 167.

[2] *J. Soc. Chem. Ind.*, 1939, *58*-(*9*), 278–83.

Lea and Nurse [1] have studied the permeability method for the determination of the specific surface of fine powders described by Carman [2] and find that when liquids are used high results are obtained when the specific surface exceeds 1,000 sq. cm. per gram. These authors have developed an air permeability method which gives satisfactory results for cements with specific surfaces up to 4,000 sq. cm. per gram. Good agreement was obtained with the results obtained by Andreason's sedimentation method. The air permeability method gives values which are satisfactorily reproducible.

The Lea and Nurse apparatus consists of a cylinder containing a rigid perforated brass plate supporting a filter paper. A known weight of the cement is filled into the cylinder and compressed to a bed of fixed depth by means of a plunger. The porosity of the bed is calculated from the density of the cement and the volume filled. The permeability apparatus is connected to a manometer and a flowmeter. The flowmeter consists of a capillary-tube 1 mm. bore with a manometer connected across its ends. Air dried and freed from carbon dioxide is forced through the cement and the manometer read for various flow rates. Calculation of the specific surface is made with the formula proposed by Lea and Nurse.

The air permeability method gives results which are about 1·6 to 1·8 times those given by the Wagner Turbidimeter. The main reason for this difference in results is due to the assumption in the turbidimetric method that the average diameter of the particles below 7·5 μ is 3·75 μ, which is higher than the true value while in the air permeability method no such assumption is made.

The air permeability method is very suitable for plant control work as the time required for making a test is about 10 minutes.

Strength Tests and Other Tests

(*a*) **Tensile Strength.** Tensile strength tests on neat cement, i.e. cement gauged with water alone, have been abandoned in nearly every country, as the tests do not give a reliable indication of the quality of a cement.

Tensile tests on a mortar composed of one part cement and three parts of standard sand and gauged with the specified amount of water are now universally adopted.

(*b*) **Compressive Strength Test.** Compressive strength tests are carried out on cubes or cylinders of set concrete made with the cement under test. The usual proportions of cement, sand, and gravel are as 1 : 2 : 4. The amount of water taken is usually equal to 0·5 to 0·6 times the weight of the cement used.

(*c*) **Soundness.** The most important method of testing the soundness (or constancy of volume during setting) of cement is that due to Le Chatelier.

[1] *J. Soc. Chem. Ind.*, 1939, *58*, 277.

[2] *Trans. Inst. Chem. Eng.*, 1937, *15*, 150; *J. Soc. Chem. Ind.*, 1938, *57*, 225.

The cement paste is filled into a small brass mould split longitudinally and having two pointers which diverge if the mould is forced open by the expansion of the cement during setting. The distance by which the pointers are forced open is taken as the expansion of the cement.

An autoclave method is also used. The cement paste is filled into cylindrical moulds of 1 sq. in. cross-sectional area and 10 in. long. The specimens after they have been subjected to the required exposure in the moist-air room or cabinet are placed in a special autoclave and subjected to the action of steam at high pressure. The average difference in the lengths of two specimens before and after treatment is known as the 'autoclave' expansion of the cement.

(*d*) **Heat of Hydration.** Heat of hydration represents the heat of hydration and solution of uncombined lime and gypsum and the heat of hydration of the main constituents of the cement. The heat evolved during the hydration of cement is of importance when large concrete masses are placed.

Takata [1] proposed a thermos-flask method of measuring the temperature rise in the heat evolution of cement, and consequently the heat of hydration can be calculated. The procedure described is mainly in accordance with the method proposed by the International Commission on Large Dams. The flask is cylindrical in form, about 7·3 cm. in diameter and 22·5 cm. in depth, and its volume about 950 ml. The test specimen of cement paste or mortar is moulded in a brass container which has an upper diameter of 6 cm. and a base diameter of 5 cm. Its depth is 14 cm. and its weight is about 930 grams. The temperature rise is measured by an electric resistance thermometer.

Davey [2] describes a method for determining the maximum temperature which can be reached in the centre of a large mass of concrete. A small sample of the concrete is prepared and placed in an adiabatic calorimeter. The temperature time curve is drawn. The temperature rise is converted into calories per gram of cement.

Carlson [3] showed by means of a conduction calorimeter that different cements may have vastly different early heat liberation characteristics.

Forbrich [4] describes a method for controlling the heat evolution of cements by addition of small quantities of active reagents. By use of suitable combinations of active reagents it is possible to control the early rate of heat liberation in any desired direction.

Woods, Steinour, and Starke [5] describe a differential heat of solution method for determining the heat of hydration of cements. The heat of solution of the original cement and of the set cement, after curing for 22 hours at 22° and thereafter at 38°, is measured in a calorimeter. The solvent employed per 3 gram of dry cement or an equivalent amount of crushed set cement is a mixture of 640 grams of 2·5 N nitric acid and 10 ml. of pure hydrofluoric acid. By an application of Hess's law of constant heat summation the heat of hydration is calculated.

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[1] Twenty-fifth General Meeting of the Association of Japanese Portland Cement Engineers, 1941.

[2] *Concrete and Constr. Eng.*, 1931, *26*, 572.

[3] *Proceedings*, Seventeenth Annual Meeting, Highway Research Board, Dec. 1937.

[4] *J. Amer. Concr. Inst.*, Nov., 1940.

[5] *Ind. Eng. Chem.*, 1932, *24*, 1207.

CHAPTER XX[3]

ELECTROLYTIC OXIDATION[1]

SECTION 1: INTRODUCTION

ELECTROLYTIC oxidation processes may be divided into two classes:

(a) Those in which the oxidation reaction is purely electrical, the anode serving merely to remove electrons from the substances being oxidized.

(b) Those in which the oxidation is brought about by a chemical oxidizing agent first formed at the anode.

These two classes differ markedly in their dependence upon experimental factors and it is therefore important that they should be sharply distinguished. Mere inspection of the oxidation equation is inadequate to decide to which class any given oxidation belongs. Thus in the oxidation of thiosulphate to tetrathionate ions the net process can be represented purely electrically, $2S_2O_3'' \rightarrow S_4O_6'' + 2e$, but the reaction actually belongs to class (b), while the oxidation of hydroquinone to quinone, which involves a decrease in the hydrogen content of the substance, $C_6H_4(OH)_2 \rightarrow C_6H_4O_2 + 2H^{\cdot} + 2e$, has many of the features of a class (a) reaction.

Oxidation processes of class (a) are usually thermodynamically reversible and give rise to a definite oxidation-reduction potential which varies with the amounts of oxidized and reduced forms of the substance present in conformity with the equation

$$\pi = \pi_0 + \frac{RT}{nF} \log_e \frac{a_{Ox.}}{a_{Red.}}$$

where $a_{Ox.}$ and $a_{Red.}$ represent the activities of the oxidized and reduced forms, n is the net change in the number of electrons as a result of the reaction, π_0 is the standard oxidation-reduction potential of the system, and R, T and F have their usual significance. On electrolysis, as soon as the anode attains a potential slightly more positive than the equilibrium value, oxidation occurs and continues with only slight change of potential until the electrolyte is poor in depolarizer and limiting diffusion conditions are reached when some other anodic process (usually oxygen evolution) must set in. Provided the current used is below the limiting value, the oxidation occurs with approximately 100 per cent efficiency, and is largely independent of experimental factors such as the nature of the anode material, current density (C.D.), temperature, and concentration and nature of electrolyte. For an unstirred electrolyte at room temperature, the magnitude of the limiting C.D. for any process is very approximately given by the formula[1]

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[1] By Dr. A. Hickling, Dept. of Inorganic and Physical Chemistry, University of Liverpool.

$$\text{C.D. (amps./sq. cm.)} = 0{\cdot}0223\ \text{DC}n$$

where C is the concentration of oxidizable substance in gram-ions per litre, D is the diffusion coefficient (usually about 1·0), and n has its former significance. Stirring of the electrolyte or increase of temperature raises the limiting C.D. considerably. Typical examples of electrolytic oxidation processes of class (*a*) are the oxidation of ferrous to ferric salts $\text{Fe}^{\cdot\cdot} \longrightarrow \text{Fe}^{\cdot\cdot\cdot} + e$, of potassium ferrocyanide to ferricyanide $(\text{CN})_6'''' \longrightarrow (\text{CN})_6''' + e$, and of cerous to ceric salts $\text{Ce}^{\cdot\cdot} \longrightarrow \text{Ce}^{\cdot\cdot\cdot} + e$.

Oxidation processes of class (*b*) are very numerous and include most of the industrially important electrolytic oxidation reactions. They are not usually thermodynamically reversible and are seldom characterized by a definite oxidation-reduction potential. The main oxidation process is frequently accompanied by side reactions, and the current efficiency, which is usually appreciably lower than 100 per cent, depends markedly and in a very complex manner upon experimental factors such as the nature of the anode material, C.D., temperature, concentration of depolarizer, *p*H of the electrolyte, presence of foreign substances, &c. The simple view that oxidations of this type are brought about by nascent oxygen formed at the anode is quite inadequate to explain the very varied and often contradictory phenomena observed in different cases, but the position has been clarified by the Hydrogen Peroxide Theory[2] which makes it possible to predict the nature of the products in any given oxidation and also to forecast the most suitable conditions to secure an optimum yield. The theory postulates that the initial anodic reaction in the electrolysis of an aqueous solution is the discharge of OH′ ions to form OH radicals which immediately combine irreversibly to form hydrogen peroxide, thus:

$$\text{OH}' = \text{OH} + e$$

followed by

$$2\text{OH} \longrightarrow \text{H}_2\text{O}_2$$

This reaction is considered to occur even at very low anode potentials and to take precedence over or to accompany nearly all other anodic discharge processes. The hydrogen peroxide will be formed as a thin layer of high local concentration on the anode surface, and in the presence of a depolarizer will bring about its own characteristic oxidation reactions. At the same time, a portion of the peroxide (its magnitude depending upon the experimental conditions) will decompose to give nascent oxygen and water, and the oxygen either directly or via the formation of oxides with the anode material may also bring about oxidation of the depolarizer. If, therefore, the chemical reactions of hydrogen peroxide, oxygen, and metallic oxides with the depolarizer are known, the nature of the electrolytic oxidation products can be predicted. Conditions favouring the stability of hydrogen peroxide, e.g. an anode material which is a poor catalyst for its decomposition, low temperature, acid solution, and high concentration of depolarizer, will favour the production of its oxidation products, while conditions accelerating the decomposition of hydrogen peroxide, e.g. the presence of catalysts for its decomposition, high temperature, alkaline solution, and low concentration of depolarizer, will increase either the yield of oxidation products due to oxygen or oxygen evolution.

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[1] *See* Glasstone and Hickling, *Electrolytic Oxidation and Reduction*, Chap. III (Chapman & Hall, 1935), for a full treatment of diffusion phenomena in electrolysis.

[2] Glasstone and Hickling, *J. Chem. Soc.*, 1932, 2345, 2800; 1933, 829; 1934, 10, 1772, 1878; 1936, 820; Hickling, 1936, 1453; Hickling and Gross, 1937, 325; Hickling and Westwood, 1938, 1039; 1939, 1109; Hickling and Richards, 1940, 256; Hickling and Rodwell, 1943, 90. For reviews, *see* Glasstone and Hickling, *Chem. Reviews*, 1939, *25*, 407; *Trans. Amer. Electrochem. Soc.*, 1939, *75*, 333.

The operation of these factors has been traced in a large number of cases,[1] such as the electrolytic oxidation of thiosulphates, sulphites, acetates, chromic salts, ester-acid salts, iodates, and formaldehyde, and from these, two illustrative examples may be taken. Thus sodium thiosulphate is readily oxidized by hydrogen peroxide to give mainly tetrathionate with a little sulphate, but is little affected by oxygen or metallic oxides. In the electrolysis of thiosulphate solutions it is found that under conditions such that hydrogen peroxide is stable, an excellent oxidation efficiency is achieved, the product being mainly tetrathionate with a little sulphate, but if conditions are such that the decomposition of hydrogen peroxide is accelerated the oxidation efficiency falls off rapidly and in the presence of catalysts such as manganous salts it may become zero, all the current then being used in oxygen evolution. On the other hand, with chromic salts in acid solution, hydrogen peroxide not only produces no oxidation but actually reduces any chromate present, although some metallic oxides can bring about oxidation to chromate. In conformity with this, it is found that in the electrolysis of chromic salts in acid solution, conditions favouring hydrogen peroxide decomposition are essential if chromate formation is to take place, and an optimum yield is obtained if the anode material is one with which oxygen can form an oxide which is an effective oxidizing agent.

The anode potential phenomena associated with electrolytic oxidations of class (*b*) are often complex, and the measured potentials during electrolysis have, in many cases, no direct connexion with the nature of the oxidation products. The Hydrogen Peroxide Theory suggests that the potentials are set up indirectly by electromotively active substances formed at the anode. Frequently the only electromotively active substance is oxygen arising from the decomposition of the hydrogen peroxide, and the anode potential will then ultimately become that of slow oxygen evolution. If, however, the rate of oxygen accumulation at the anode is slow, e.g. in the presence of a good depolarizer, the attainment of the oxygen evolution potential may be preceded by one or more low potential stages corresponding to the formation of various oxides with the anode material. In some cases the chemical oxidation of the depolarizer may lead to the momentary formation of electromotively active radicals which set up a potential characteristic of one of the reactions taking place; this occurs, for example, in the electrolysis of acetates and acid-ester salts in aqueous solution. From the above summary it will be seen that the anode potential in oxidations of class (*b*) is a resultant rather than a controlling factor of the reaction; in spite of this, observation of the potential phenomena is often useful in throwing light upon the mechanism of a particular oxidation.

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[1] *Loc. cit.*

Laboratory investigation of electrolytic oxidation reactions is usually directed to the elucidation of the mechanism of a particular process, and the discovery of the conditions necessary to give an optimum yield of a desired product. Such investigation follows two main lines:

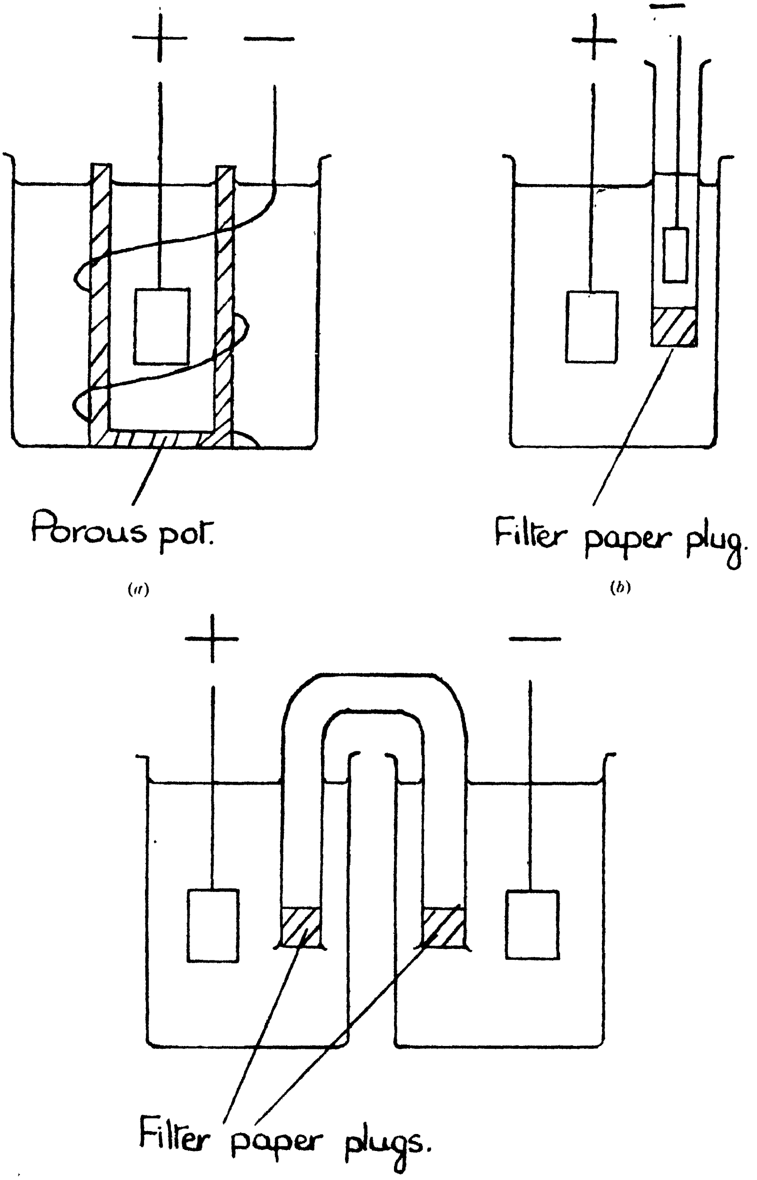
(1) The measurement of the current efficiencies of the anodic reactions under various experimental conditions.

(2) The observation of the concomitant anode potential phenomena.

SECTION 2: EXPERIMENTAL METHODS

Electrodes. In general there is a tendency for an anode to go into solution under the influence of the current passing, and the choice of anode is therefore limited to those materials which can be made passive under the particular experimental conditions employed. In alkaline solution most metals other than those forming acidic oxides can be used, but in neutral and acid solution the most generally useful anodes are smooth platinum, platinized platinum, battery carbon and graphite, nickel, lead, and gold. It is sometimes useful to employ preformed oxide anodes, such as lead and manganese dioxides, and these can be conveniently formed as adherent coatings on platinum by anodic deposition from solutions of the appropriate salts. For electrodes up to about 2 sq. cm. in area, the anode materials are best employed in the form of spirally wound wires or thin straight rods, sealed either directly or by means of sealing-wax into supporting glass tubes, into which the connecting-leads are introduced and contact made either by mercury or by a wrapped or soldered joint. Larger electrodes are best cut in a rectangular form from thin flat sheets of the anode materials, a small projection being left on the edge of each electrode for mounting it in the above way. Cylindrical and gauze electrodes, such as are often used in electroanalysis, suffer from the disadvantage that the precise area utilized in electrolysis is difficult to assess and hence the C.D. cannot be accurately worked out. Since in electrolytic oxidation processes the cathode and catholyte are usually separated from the main cell by a porous partition, the nature of the cathode is not important; on a small scale platinum is usually employed.

Separation of Anode and Cathode Compartments. To avoid reduction of oxidized products at the cathode, it is frequently necessary to have the anode and cathode in compartments separated by a porous diaphragm. A common way of achieving this on a laboratory scale is by the use of cylindrical porous pots such as are employed in Daniell and Leclanché cells. The pot may hold either anolyte or catholyte and is mounted in a larger vessel which forms the second compartment. Such an arrangement has a very low electrical resistance when the pot is saturated with electrolyte, and will pass high currents, but it has a number of defects which render it somewhat unsuitable for precise investigations. Thus the porous pot permits a certain amount of mixing of anolyte and catholyte in long electrolyses, it soaks up a considerable volume of electrolyte which is not recoverable, it is very difficult to clean and may introduce impurities into the electrolyte, and for many purposes it is inconveniently bulky. A much more satisfactory arrangement, where only small currents (up to 1 amp.) are used, is as follows. The cathode compartment may take the form of a short straight glass tube (about 2 cm. in diameter) dipping into the anolyte and having its lower end closed by a filter paper plug. This plug



(a) (b)

(c)

FIG. 1 (XX^{a})

Methods of separating anode and cathode compartments

is made by taking a long strip of filter paper about an inch wide and rolling it up on itself to form a solid cylinder rather greater in diameter than the cathode tube; several lengths of paper may be consecutively employed if necessary. The cylinder is then soaked in the supporting electrolyte to be used and screwed (by rotating in one direction only) into the cathode tube; this procedure both secures a tight fit and closes up the spaces between successive layers of paper. When the plug is half-way in, the projecting portion is then cut off cleanly with a razor, level with the bottom of the tube, leaving a smooth hard surface. This arrangement has a reasonably low electrical resistance but completely prevents mixing of anolyte and catholyte even over prolonged periods; diffusion into the plug is extremely slow and there is practically no tendency for it to take up further electrolyte. If kept under water or electrolyte between electrolyses, the plug may be repeatedly used over a period of months; at the same time it is readily renewable if it becomes contaminated with impurities, and a set of several cathode tubes may be made for use with different electrolytes. The cathode compartment can be mounted in any convenient position in the cell and requires only a few millilitres of electrolyte to fill it. Where it is desired to study both anodic and cathodic reactions, two separate vessels may be employed, joined by a siphon (formed from a wide U-tube) filled with an indifferent electrolyte and stopped at the ends with filter paper plugs made in the above manner. The various methods of separating anode and cathode which have been described are represented in Fig. 1 (XX^3), *a*, *b*, and *c*.

On a technical scale prevention of cathodic reduction is achieved by a variety of methods,[1] e.g. by the use of mechanical diaphragms of asbestos, cement, electro-filtros, &c., or by employing chemically formed membranes on the cathode such as chromic chromate, produced by adding a soluble chromate to the electrolyte, or by using a very small cathode so that the limiting current for the diffusion of the oxidized substance to the cathode is small compared with the total current passing; such methods are seldom advantageous in laboratory investigations.

Agitation of Electrolyte. It is frequently desirable to have the anolyte stirred. This both renders diffusion conditions at the anode more reproducible and increases the limiting C.D. for any given process; where the depolarizer is present as an emulsion or suspension, stirring is essential. It may be provided either by an independent stirrer, usually of glass and of the screw or paddle type, or by rotating the anode itself. In the latter case the problem arises of the mounting of the anode so as to secure satisfactory electrical contact with the current supply. A very satisfactory form of mounting is shown in Fig 2 (XX^3). The pulley (for a string drive from an electric motor) is attached to a length of wide-bore capillary tubing which is carried in a bearing made of either glass or brass tubing. At its lower end the capillary-tube is fastened by a short length of pressure tubing (wired-on) to a watchmaker's chuck which clamps the spindle of the electrode; a second short bearing serves to maintain the alignment of the spindle. The capillary-tube is filled with mercury, which makes contact with the chuck, and the current is led in by a stationary wire dipping into the top of the tube. The bearings may be lubricated with vaseline, and speeds up to 500 r.p.m. can be used without difficulty. If the anode is not one which can be satisfactorily provided with a spindle-like extension, it may have a tab projecting out of the liquid and fastened by a nut and bolt to a suitable metal holder held in the chuck.

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[1] *See* Glasstone and Hickling, *Electrolytic Oxidation and Reduction*, 1935, p. 345.

Temperature Control. As temperature often has an appreciable influence upon electrolytic oxidation processes, it is usually desirable to have it maintained constant within ± 1°. Very small cells may be directly introduced into suitable temperature baths, but with larger cells it is usually best to insert a glass spiral into the cell itself, through which water can be circulated. Where high currents are employed and the energy dissipation

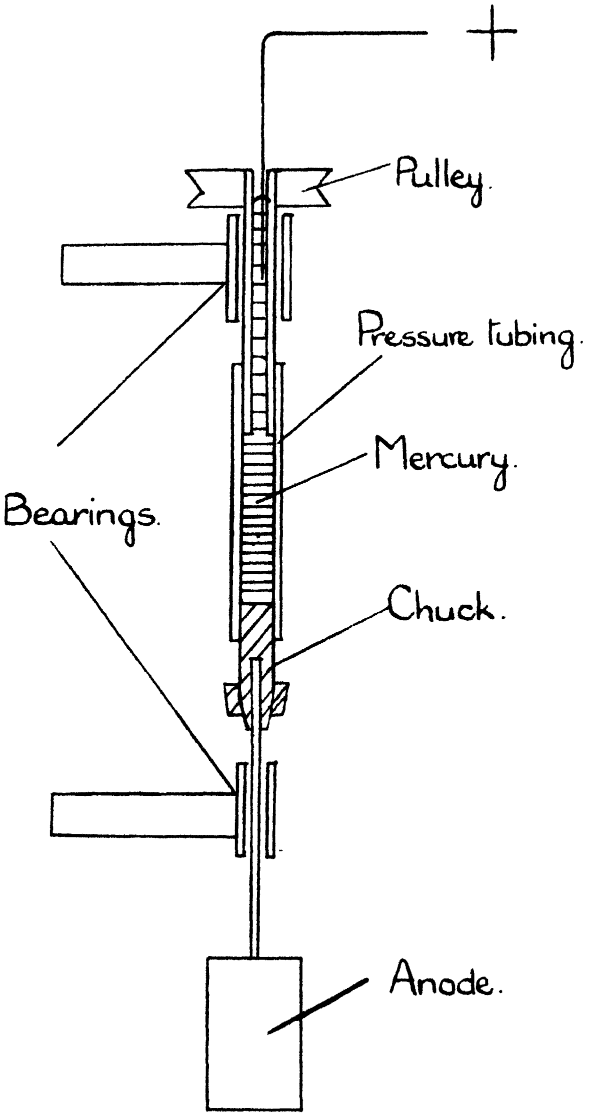

FIG. 2 (XX[3])
Mounting of rotating anode

in the cell is considerable, it may be necessary to circulate water at a temperature several degrees lower than that required in the cell.

Collection of Gaseous Products. It is sometimes necessary to collect for examination gaseous products formed at the anode. Where the cell is small and can readily be fitted with an airtight stopper this introduces no difficulty, but where the cell is large and particularly when it is fitted with cathode vessel, stirrer, thermometer, cooling-coil, &c., the problem cannot be solved so simply. One way of meeting it is shown in Fig. 3 (XX^3) which depicts a cell used in the investigation of the electrolytic oxidation of formaldehyde.[1] The anode may be partially enveloped by a glass hood connected by capillary tubing to a gas-measuring burette, which is also connected to a small mercury trough. Initially the anolyte is drawn up so as completely to fill the hood; from time to time as the gaseous products of anodic oxidation collect in the hood, they are drawn off, their volume measured, and samples collected via the mercury trough for subsequent examination.

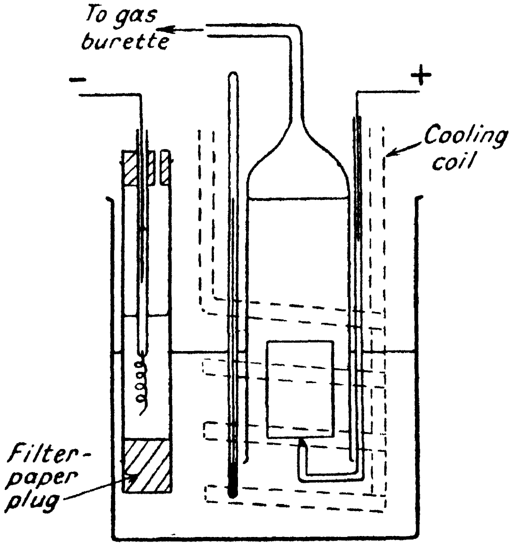

FIG. 3 (XX^3)
Cell for electrolytic oxidation of formaldehyde—collection of gaseous products

General Assembly of Cell. The actual nature of the electrolytic cell will obviously vary widely according to the amount of electrolyte to be used, whether a diaphragm is employed, whether stirring is necessary, whether gaseous products are to be collected, &c. In general a squat jar or beaker of suitable capacity forms a satisfactory outer vessel. It is best stood on a block with the accessory apparatus (cathode vessel, stirrer, electrodes, &c.) independently clamped and dipping into it, so that by removing the block the vessel may be withdrawn or put into place with the minimum of disturbance. A generally useful electrolytic stand of robust construction may be made by clamping together side by side two heavy retort stands and fastening to them at the top a bakelite strip carrying terminals for connexion to the current supply. To avoid a congestion of clamps above the cell, the items of accessory apparatus may be conveniently mounted through holes in a wooden bridge clamped between the two stands,

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[1] Hickling and Rodwell, *J. Chem. Soc.*, 1943, 90.

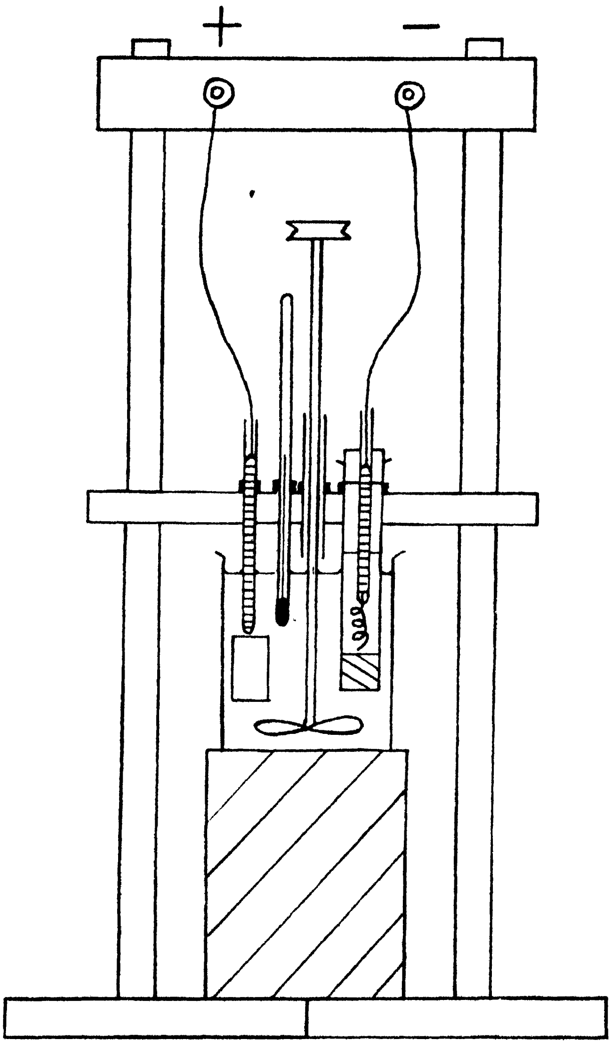

FIG. 4 (XX[3])
Electrolytic stand and general assembly of cell

and held in place by slips of rubber tubing. Connexion to the electrodes may be made by short lengths of wire from the permanent terminals. Fig. 4 (XX[3]) shows an electrolytic stand of the above type with a cell fitted with cathode compartment, stationary anode, independent stirrer, and thermometer.

Current Efficiencies

The current efficiency for any process of electrolytic oxidation is the fraction of the total quantity of electricity passed which is used in bringing about that process, and it is usually expressed as a percentage. Where it is only required to find the overall oxidation efficiency, this may be conveniently done by measuring the amount of oxygen evolved at the anode and comparing it with that evolved in an oxygen coulometer in series with the electrolytic cell. This method has the advantage that any variation of current efficiency with time can readily be followed, but it is not very generally applicable since, in all but the simplest cases, there may be a number of alternative anodic oxidation reactions, and the method gives no indication of the individual efficiencies of these. In most cases it is necessary to pass a definite quantity of electricity through the electrolytic cell, and then to carry out a complete quantitative analysis of the anodic products ; from the amount of each formed, compared with the theoretical amount if all the current had been devoted solely to its production, the current efficiency of each process can readily be calculated. In certain cases it is desirable also to estimate the amount of depolarizer used up to ascertain the quantitative relation between it and its oxidation products.

The amount of electricity to be passed is in general decided on grounds of convenience ; it should be such as to give readily estimable amounts of products and reasonable times of electrolysis at the currents to be used. The amount of electricity may be measured by a coulometer in series with the cell, but in general, once the effect of varying quantities of electricity has been established, it is preferable to pass a constant quantity in each electrolysis, and this may be conveniently determined by measuring the current with an ammeter (previously calibrated against a copper coulometer) and controlling the time of electrolysis.

Factors which it may be desirable to vary in order to observe their effects upon the current efficiencies of the anodic processes may include C.D., time of electrolysis, nature of anode material, concentration of depolarizer, temperature, *p*H of electrolyte, addition of foreign substances to the electrolyte, and anode potential. In connexion with these factors a number of practical points may be mentioned. Variation of C.D. may be achieved either by alteration of current (with consequent change in time of electrolysis) or by change of anode area. Where only a small range of C.D. is to be explored the first is usually the more convenient procedure, but where a large C.D. range is to be investigated or where time of electrolysis is important the second method is generally preferable. In working with different anode materials, the exact state of the anode surface is often of predominating importance ; it is essential, therefore, that systematic methods of cleaning and preparing the electrodes be adopted if reproducible results are to be obtained. The hydrogen-ion concentration of the electrolyte often has a very important influence upon the current efficiencies of oxidation processes, and since the anolyte usually becomes acid on electrolysis, owing to the discharge of hydroxyl ions, it is necessary that its *p*H value should be accurately controlled. For acid and alkaline electrolytes this may generally be satisfactorily achieved by using the depolarizer in sulphuric acid or sodium hydroxide solutions of definite strengths, while for conditions near the neutral point phosphate buffers are often convenient since they are relatively inert and not themselves very liable to oxidation. Foreign substances which may affect electrolytic oxidation processes fall into a number of categories. Firstly, catalysts for hydrogen peroxide decomposition often influence markedly the anodic reactions; they include such substances as manganese, lead, silver, iron, cobalt, and copper salts, the corresponding metallic oxides, and finely divided elements such as silver and carbon. Secondly, in oxidation processes brought about by oxygen, certain substances can act as positive catalysts or 'oxygen carriers'; they are generally inorganic ions capable of undergoing reversible oxidation and reduction and include manganese, chromium, cerium salts, &c. Thirdly, certain anions, particularly fluoride and to a less extent perchlorate, seem to have a specific action in improving the efficiencies of some electrolytic oxidation processes. Fourthly, catalytic poisons, such as mercuric cyanide and arsenious oxide, may change the anodic reactions in some cases. Fifthly, where the depolarizer is the anion of a slightly dissociated substance any inert salt may influence the oxidation processes by modifying the transport by the current of the depolarizer ions to the anode. The control and variation of anode potential is dealt with later.

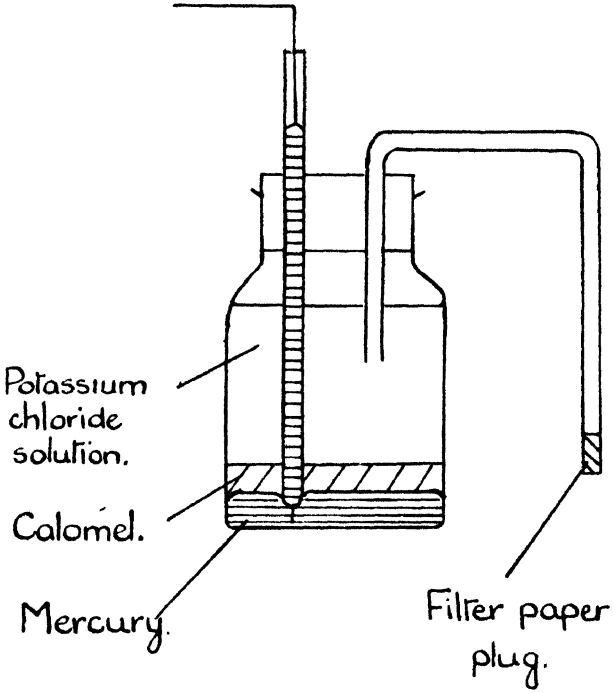

FIG. 5 (XX[8])
Calomel reference electrode

Anode Potentials

As has been already indicated, observations of anode potential are often useful for throwing light upon the mechanism of anodic processes. Such observations normally follow two complementary lines :

(i) The anode potential may be measured at different times during the electrolyses at constant C.D.s ; this method is particularly valuable where the anode undergoes progressive polarization.

(ii) The way in which the anode potential varies with C.D. under various conditions may be ascertained by a series of instantaneous observations and the C.D.-potential curves drawn ; this method is rapid but the results may be difficult of interpretation if the anode potential changes progressively with time of polarization.

The measurement of anode potentials involves a number of practical problems, viz. the choice and construction of a suitable reference electrode, its connexion to the working anode, and the measurement of the e.m.f. between the anode and reference electrode. The most generally useful reference electrode is the saturated calomel electrode, and a convenient form of it is shown in Fig. 5 (XX[3]). The electrode is set up in a small jar, and the tip of the connecting-siphon is stopped with a filter paper plug. To avoid resistance error in the potential measurement (*vide infra*), it is desirable that the tip of the siphon be brought as close as possible to the working anode. This is best achieved by a modification of the original Luggin capillary [1] as shown in Fig. 6 (XX[3]). An open tube is drawn out at its lower end into a bent capillary about 1 mm. in diameter and fixed in position pressing lightly upon the anode ; into this tube is introduced the siphon of the calomel electrode when observations are to be made. If it is necessary to avoid all risk of diffusion of potassium, mercurous, and chloride ions into the anolyte, connexion may be made as shown in Fig. 7 (XX[3]) by an

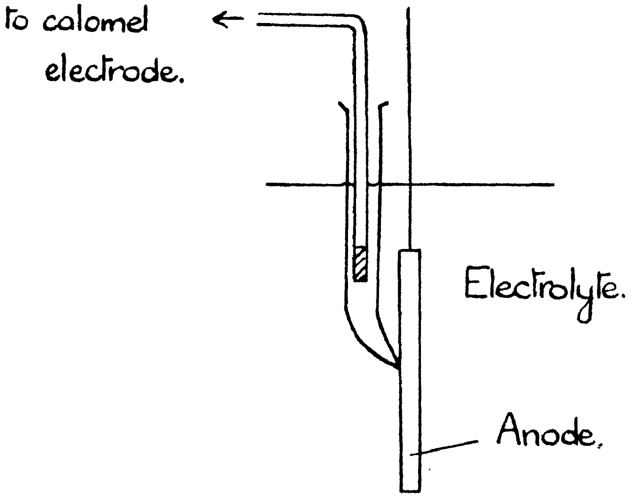

FIG. 6 (XX[3])
Modified Luggin capillary

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[1] *Z. physik. Chem.*, 1900, *32*, 208 ; Knobel, Caplan, and Eiseman, *Trans. Amer. Electrochem. Soc.*, 1923, *43*, 55.

additional salt bridge filled with a suitably inert electrolyte. As electrolytic oxidation potentials are seldom more reproducible than 1–2 centivolts, liquid junction potentials can usually be neglected.

The measurement of the true e.m.f. between a working electrode and a reference electrode involves a considerable practical difficulty, and several methods of operation have been devised and will be considered in turn.

Direct Method. In this method, the combination of the working and reference electrodes is connected directly to a potentiometer and the e.m.f. is measured while the polarizing current is flowing in the electrolytic cell. The potentiometer-voltmeter method [1] of measurement is usually employed, and a particularly convenient and simple circuit [2] is shown in Fig. 8 (XX^3). The potentiometer consists of two low resistance circular rheostats A and B, such as are used in radio-construction, joined in series and connected to an accumulator battery C. One of the rheostats serves for coarse and the other for fine adjustment of voltage ; their resistances may be in the ratio of 5 : 1 and 50 and 10 ohms are suitable values. An accurate voltmeter V is permanently connected between the movable arms of the rheostats, which are also connected via a push-button or tapping key K and a galvanometer B to the unknown e.m.f. X. G, which serves as a null point indicator, may conveniently be replaced by a spring-controlled microammeter. A and B

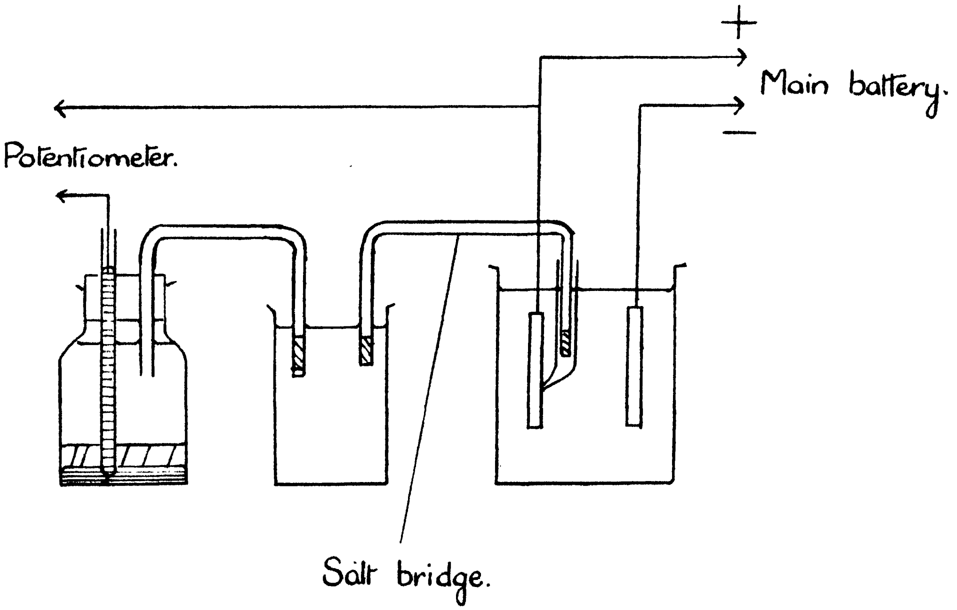

FIG. 7 (XX^3)
Measurement of anode potential

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[1] Sand, *J. Chem. Soc.*, 1907, *91*, 380 ; *J. Soc. Chem. Ind.*, 1911, *30*, 3T ; Hildebrand, *J. Amer. Chem. Soc.*, 1913, *35*, 847.

[2] This circuit is a modification of one originally suggested by T. B. Smith, *Trans. Faraday Soc.*, 1928, *24*, 216.

are adjusted until G shows no current on depressing K, and the e.m.f. is then read directly from the voltmeter V.

In the direct method as above described there is a source of error which may under certain circumstances be exceedingly troublesome. If there is any appreciable resistance between the tip of the tube connecting the reference to the working electrode and the point at which the latter is connected to the potentiometer system, a fall of potential equal to the product of the resistance and the current flowing in the electrolytic cell will be included in the measured potential of the working electrode. Now although any such resistance is minimized by the use of the modified Luggin capillary described above, it is impossible to eliminate it entirely. There is always present a certain surface resistance at a working electrode due to gas evolution and depletion of electrolyte in the diffusion layer, and in the case of an anode the surface may become covered with a poorly conducting oxide film. In view of these factors, potential measurements by the direct method, at any but the most minute currents, may involve a considerable error, e.g. at 0·2 amp. a surface resistance of 5 ohms would lead to an error of 1 volt in the measured potential. It is not possible to give any precise guide as to the C.D. range over which the direct method is likely to give accurate values, but general experience has shown that with highly conducting electrolytes and under conditions such that film formation does not occur on the anode, the resistance error is small up to a C.D. of about 0·01 amp./sq. cm.; at higher C.D's it may become very large.

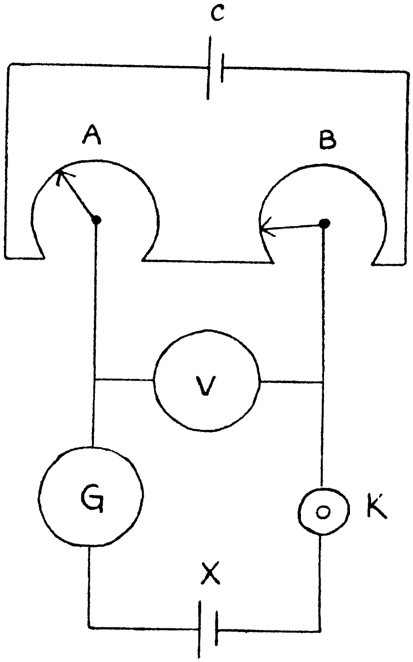

FIG. 8 (XX³)
Simple potentiometer-voltmeter

Commutator Method. To eliminate the resistance error described above, it is apparent that the polarizing current in the electrolytic cell must be momentarily switched off while the potential measurement is being made. This was first attempted by Le Blanc [1] who used a vibrating tuning fork which alternately connected the working electrode to the polarizing circuit and to the potentiometer system. Newbery and other workers [2] subsequently used high-speed rotating commutators to achieve the same object. These early methods, however, led to erroneous results because the potential measured was the average potential during the ' off ' period, and since many electrode potentials decay very rapidly on interruption of the polarizing current, this average value might be quite different from that at the instant of switching off. In the method as perfected by Glasstone[1] this difficulty is overcome by measuring the almost instantaneous potentials of the electrode at chosen fractions of a second after the polarizing circuit is broken, and the results are extrapolated to give the value at zero time, i.e. at the instant of switching off the polarizing current. Glasstone's commutator is shown in Fig. 9 (XX^3). It consists of a cylinder 3 in. long and 1½ in. in diameter, divided into two similar parts, A and B, which can be fixed in different positions relatively to one another on the axis of revolution CD. The unshaded portions represent insulated parts of the commutator, whilst the shaded parts are metallic; connexion is made from the polarizing circuit and from the potentiometer to the movable contact makers *a* and *c*, whilst *b* is connected to the working electrode. By moving *a*, the electrode can be connected with the polarizing circuit for any desired portion of a complete circle, whilst by moving B relative to A round the axis CD, and also moving *c*, the electrode can be connected to the potentiometer at any section of a cycle for any desired interval of time. The commutator is coupled directly to a variable speed electric motor, a small revolution counter being attached to the shaft of the motor for calculating the speed. In a typical application, using two motor speeds and two positions on the commutator, potential measurements can be made 0·002 seconds, 0·004 seconds, 0·006 seconds, and 0·012 seconds, after interruption of the polarizing current and the results extrapolated to zero time.

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[1] *Z. physik. Chem.*, 1890, *5*, 469.

[2] Newbery, *J. Chem. Soc.*, 1914, *105*, 2422; 1916, *109*, 1051, 1066; 1922, *121*, 7; Sand *et al.*, *ibid.*, 1923, *123*, 456.

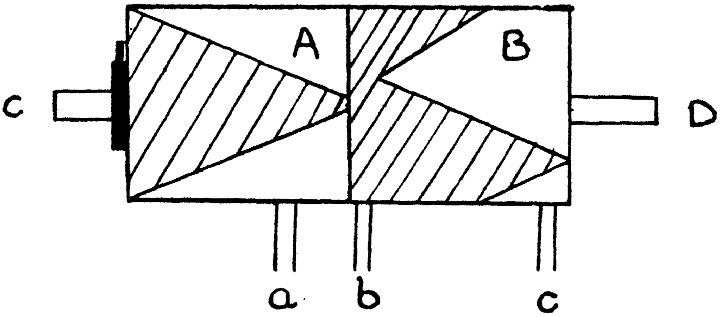

FIG. 9 (XX^3)
Glasstone's rotating commutator

While the perfected commutator method is satisfactory in principle, it is in practice attended by a number of difficulties which may be briefly summarized:

(i) The minimum 'off' period which can be conveniently obtained with a mechanical commutator is of the order of 0·001 seconds, and this is too long to permit of accurate extrapolation where the rate of electrode potential decay is rapid.

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[1] *Ibid.*, 1923, *123*, 2926; 1924, *125*, 250. *See also* Knobel, *J. Amer. Chem. Soc.*, 1924, *46*, 2613; Sand, Grant, and Lloyd, *J. Chem. Soc.*, 1927, p. 378. For a criticism of commutator methods, *see* Ferguson, *Trans. Amer. Electrochem. Soc.*, 1939, *76*, Preprint 14.

(ii) The current reading with the commutator in operation is in general different from that when it is stationary, and it is therefore doubtful what value is to be assigned to the polarizing current.

(iii) It is uncertain to what extent the electrode potential may be affected by induced currents due to repeated make and break of the circuit.

(iv) The method is cumbersome, requiring a minimum of four observations for each potential, and involving frequent mechanical adjustment of the commutator. Furthermore, incidental difficulties due to wearing of the contacts, electrical leakage, and variable motor speed, are of frequent occurrence.

Interrupter Method. To eliminate the above difficulties, Hickling[1] has devised a completely new method. This utilizes an electrical interrupter, free from mechanical moving parts, whereby the polarizing current can be stopped for any chosen period from approximately 10^{-5} seconds upwards, with any desired frequency, the potential being measured by a special potentiometer which is left in permanent connexion with the electrode and designed to measure transient maximum and minimum voltages. In the absence of any effect due to induced currents, the maximum value recorded by the potentiometer should be the same as that obtained by the direct method, as is usually found to be the case, while the minimum value should be a measure of the potential at the end of the ‘ off ’ period. When a very short time interval is utilized this is found to be practically the same as the true electrode potential except with the most rapid depolarization processes. In the latter case measurements with a number of different time intervals,

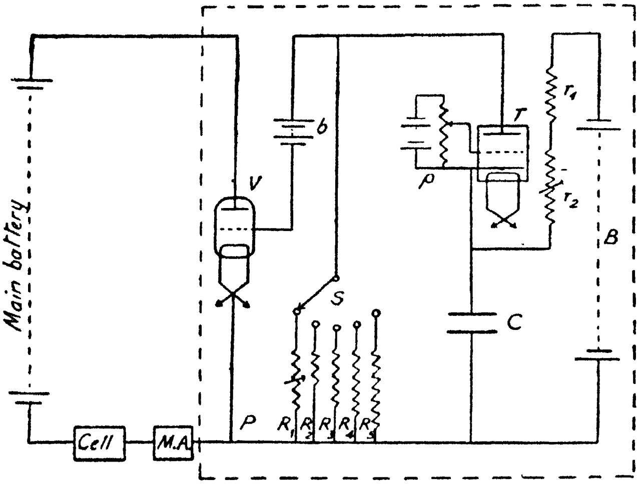

FIG. 10 (XX[3])
Interrupter circuit

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[1] Hickling, *Trans. Faraday Soc.*, 1937, *33*, 1540; Hickling and Salt, *ibid.*, 1941, *37*, 450.

obtained by the simple rotation of a dial, may be made, and extrapolation to zero time carried out. If desired the decay of the electrode potential can be followed over a whole range of times up to 10^{-1} seconds. With the shorter time intervals, the current readings with the interrupter on and off are not appreciably different.

The circuit is shown in Fig. 10 (XX^3), the interrupter embodying the components enclosed by the dotted square. The method of working is as follows: The battery B (72-volt dry battery) charges up the condenser C (0·5 microfarad) through the resistances r_1 (50,000 ohm safety resistance) and r_2 (1 megohm variable resistance), and when the condenser reaches a sufficient potential, the thyratron[1] T (Osram GT.5E) flashes over and permits the condenser to discharge through one of the resistances R_1, R_2, R_3 . . ., selected by the rotary switch S (Muirhead, 5-C-4). This, however, is included in the grid circuit of the triode valve V (Osram PX25, or several such valves in parallel) which carries the main current, and the condenser discharge has therefore the effect of imparting momentarily a high negative bias to the grid of the valve and thus preventing the passage of current. The process then repeats itself indefinitely. The voltage at which the thyratron flashes over is adjusted to the maximum voltage of the battery B by means of the biasing unit *p*, consisting of a 4·5-volt dry battery and a 100,000-ohm potentiometer; *b* is a 4·5-volt dry battery which serves to keep the grid of V slightly negative under all circumstances. The main current is varied as desired by changing the filament current of V; this is conveniently done with a Variac transformer.

The frequency of interruption is controlled by r_2. Its exact value is immaterial but it is advisable in all cases to keep the time for which the current is on much larger than the period of interruption, so that the milliammeter measuring the current gives its true value and not any mean figure, and this can readily be achieved even with the longest time intervals, by working at a frequency of interruption of about 1 per second. The duration of any interruption of current depends upon the time taken for the voltage of the condenser C to drop by a given amount and is therefore directly proportional to the value of the resistance (R_1, R_2, R_3 . . .) through which it discharges if other factors are maintained constant. These other possible variables, which determine the absolute time of interruption, are (*a*) the capacity of C, (*b*) the voltage of B, and (*c*) the grid voltage at which V ceases to pass current (cut-off voltage); (*a*) and (*b*) are normally constant, and (*c*) is constant for a given plate potential, i.e. for a steady voltage of the main battery (200 volts is a convenient value); (*c*) varies, but only slightly, with filament temperature (i.e. when different currents are used). Where it is only desired to measure an electrode potential, it is unnecessary to know the absolute times of interruption of the current; the resistances R_1, R_2, R_3 . . . can then be provided by a single calibrated rheostat of the radio type (1,000 ohms is a convenient value) and the minimum potentials measured for various settings and extrapolated to zero resistance. If it is desired to follow the decay of the potential over a long period, a bank of non-inductive fixed resistances, varying from 25 to 250,000 ohms, may be used and the interrupter may be calibrated as follows. The cell in the circuit is replaced by a condenser shunted by a resistance, part of which is included in the main current path so that the condenser is charged to a low voltage when the current is flowing. The maximum and minimum voltages across the condenser are then measured for all settings of the interrupter. Hence, applying the formula for the discharge of a condenser $t = \mathrm{RC} \log_e \mathrm{V}_1/\mathrm{V}_2$ the time of each interruption can be directly found.

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[1] The thyratron valve or gas-filled relay, which is essentially a trigger device, has many possible physico-chemical applications. For a useful account of its construction and properties, *see* Lewer and Dunham, *G.E.C. Journal*, 1932, Nos. 2 and 3; *see also Physico-Chemical Methods*, Vol. I, p. 189.

The special potentiometer[1] for the measurement of transient maximum and minimum voltages also employs a thyratron valve. Its operation depends upon the fact that the thyratron passes no current if the grid is more negative than a certain value, dependent upon the plate potential, and that this critical point is very sharply defined. If the thyratron is adjusted to the critical point, and then an unknown e.m.f. opposed by an ordinary potentiometer is introduced into the grid circuit, the critical adjustment will be restored when the potentiometer reading is equal to the unknown potential. If the unknown e.m.f. is varying and is connected so as to make the grid of the thyratron more negative than the critical value, then it is apparent that the potentiometer will measure its minimum value, while if it is introduced so as to make the grid more positive, the maximum value will be recorded. For convenience in use it is desirable that the thyratron should be automatically reset several times a second, and that the critical point should be clearly indicated in a simple manner. The circuit employed is shown in Fig. 11 (XX^3). The condenser C (0·5 microfarad) is charged by the battery B (30-volt dry battery) through a resistance R (25,000 ohms), and when it attains a sufficient potential it discharges through the thyratron T (Osram GT1A), producing a sharp click in the low-resistance loudspeaker S. The grid circuit of the thyratron includes a resistance r (10,000 ohms) which serves to limit grid current, a small potentiometer unit p (4-volt dry battery with 5,000- and 100-ohm radio potentiometers connected across it in series) for adjusting the grid potential to the critical value, and switching arrangements S_1 and S_2 by means of which the unknown potential X and the opposing potentiometer P can be either excluded from the grid circuit or introduced in any order; it is also arranged, as shown, that in opening S_1 or S_2 the current supply to the thyratron is broken. In using the instrument, S_2 is first closed and p adjusted until the grid attains the critical potential as indicated by a slow regular ticking from the loudspeaker; on one side of the critical point there is silence, and on the other the ticking rapidly merges into a continuous buzzing sound. S_2 is then opened and S_1 closed and the critical point again found by adjusting the main potentiometer P; according as S_1 is to the left or to the right, the minimum or maximum value of the unknown potential X will be read from the potentiometer. Measurements can readily be made to 0·005 volt, and if large-capacity accumulators are used for the heating of the thyratron filament, the drift of balance point can be made very small (less than 0·01 volt in several hours) obviating the need for frequent adjustment of p. The grid current taken by the thyratron in the vicinity of the balance point is of the order of 1 microamp.

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[1] Hickling, Hickling, and Salt, *loc. cit.*; *see also* Hickling and Bruce, *J. Sci. Inst.*, **1938**, ***15***, **22**.

In using the thyratron potentiometer in conjunction with the interrupter, the anode to cathode resistance of the electrolytic cell should not exceed about 1,000 ohms, and the potentiometer leads should be kept as short as possible and free from inductance to avoid pick-up from the interrupter circuit. The duration of the shortest time interval for which satisfactory potential measurements can be made depends to some extent on the circuit arrangements ; it can be tested by measuring the e.m.f. across a combination of a standard cell and a non-inductive resistance, through which the interrupted current is flowing. The minimum potential as measured by the potentiometer should be that of the standard cell alone, and this is usually found to be the case down to times of the order of 5×10^{-5} seconds.

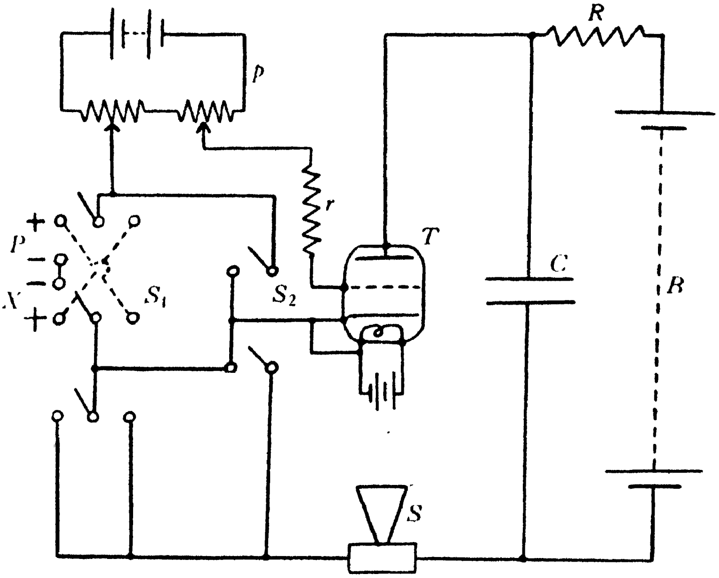

FIG. 11 (XX[3])
Thyratron potentiometer

The Control of Anode Potential

It was at one time thought that the oxidizing power of an anode was proportional to its potential, although it now appears very doubtful whether any such direct connexion exists in the case of what have been termed class (*b*) oxidations. Nevertheless, it may sometimes be desirable to ascertain the influence of anode potential by carrying out a number of electrolyses at different fixed anode potentials. This may be achieved by manual variation of the electrolytic current so that the potential of the anode with respect to the reference electrode is maintained at a fixed value throughout an electrolysis, the quantity of electricity passed being measured by a coulometer ; manual control is, however, very tedious and may be difficult if the anode potential tends to change rapidly. A device called a potentiostat has recently been described[1] whereby the potential of a working electrode can be fixed at any desired arbitrary value, and it would seem to have valuable applications in the exploration of electrolytic oxidation processes. The circuit of the potentiostat is shown in Fig. 12 (XX[3]) and the method of working is as follows. Direct current from any suitable source (battery or rectifier) is fed to the electrolytic cell through the large triode valve V_1. A heavy negative bias is imposed on the grid of this valve by the battery B_1 so that initially no current will pass. The grid circuit, however, includes a large condenser C, which is gradually charged up through the resistance R, and the condenser voltage opposes the fixed negative bias on the valve. Thus the current through the electrolytic cell tends continually to increase, and, if no other factor intervened, would rise to the maximum value which V_1 can pass. The condenser, however, can discharge through the second valve V_2 which acts as a switch, its operation being controlled, via a thyratron circuit, by means of the potential difference between the electrode which is being studied and the reference electrode. The thyratron T is supplied with alternating current, so that it is automatically set 50 times a second, and the grid is adjusted to the critical tripping voltage by means of the automatic biasing potentiometer r_1-r_2. Into the grid circuit of the thyratron is also introduced an external potentiometer P, connected so as to make the grid more negative, and, in opposition to this, the combination of the working electrode and the reference electrode. It

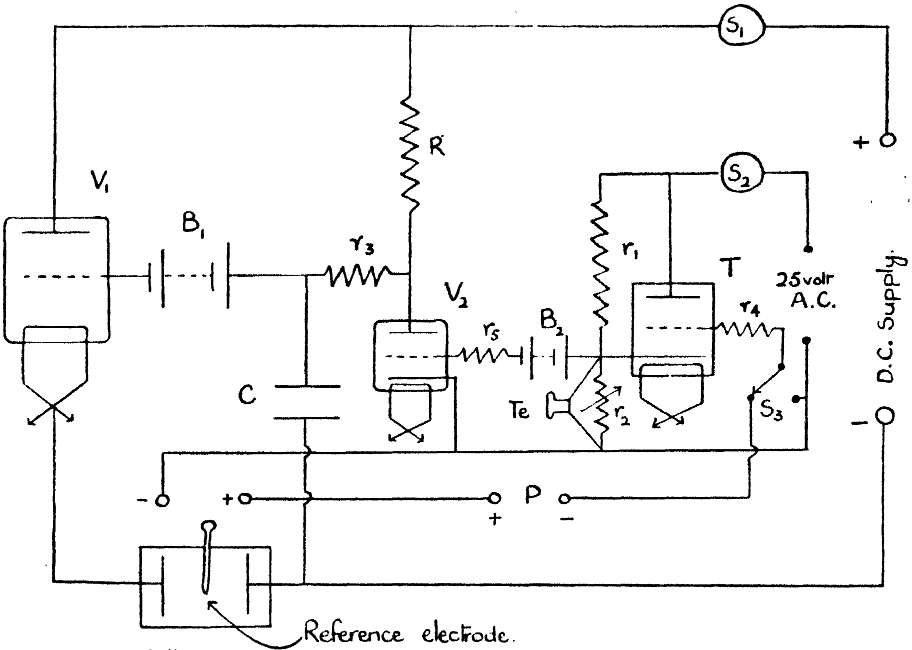

FIG. 12 (XX[3])
Circuit of the potentiostat

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[1] Hickling, *Trans. Faraday Soc.*, 1942, *38*, 27; the circuit described is an improved form of that originally published. *See also* Lingare, *Ind. Eng. Chem. Anal.*, 1945, *17*, 332.

follows, therefore, that no discharge will take place in the thyratron until the potential difference between the working and reference electrodes is equal to the e.m.f. derived from the external potentiometer P. The valve V_2 is ordinarily biased by the battery B_2 so that it will pass no current, but when the thyratron trips, the voltage across r_2, which is included in the grid circuit of the valve, renders V_2 conducting and hence the condenser C can partially discharge and the main current through the electrolytic cell will drop. Hence on switching on the apparatus, the current will rise until the working electrode has a potential relative to the reference electrode equal to the voltage set upon the potentiometer, and the current will then be automatically controlled so that this potential is indefinitely maintained. If no electrode process is possible at the arbitrarily fixed potential then the thyratron will operate continuously and the current through the cell will be zero. If, on the other hand, some electrolytic process is possible, then the limiting current for that process will pass.

The potentiostat may be constructed as a compact unit working from the A.C. mains, with terminals for external connexion to the D.C. source, the potentiometer and the electrolytic cell. Suitable values of the various components are as follows. The maximum current which the potentiostat can control is limited only by the anode current which the valve V_1 can pass; with two Osram PX25 valves in parallel and a 200-volt main battery currents up to 0·3 amp. are possible. The resistances are R 2 megohms, r_1 5,000 ohms, r_2 400 ohms (variable), r_3 25,000 ohms, r_4 0·5 megohm, r_5 1 megohm. C is an 8 microfarad electrolytic condenser. B_1 and B_2 are 60 and 9 volts respectively; if desired they may be provided by small separate rectifier units instead of bias batteries. The choice of the valve V_2 is not in any way critical, and almost any thermionic valve which requires only a small negative bias to stop the plate current completely will serve; in the circuit described a screened grid valve, Osram MS4B, is used with the plate and screen connected together. T is an Osram GT1C thyratron, supplied with 25 volts A.C. from a mains transformer, separate windings of which also supply the heater currents for the valves and thyratron. S_1 and S_2 are on-off switches, and S_3 is a two-way switch which makes it possible to check the thyratron balance point without disturbing external connexions. To give an audible indication when the thyratron is tripping, a high resistance telephone Te is connected across r_2, and the thyratron is initially set by adjusting r_2 until an intermittent buzzing is obtained with the grid circuit closed (i.e. with S_3 to the right). Once adjusted the thyratron should need no further attention provided the A.C. mains voltage is reasonably steady, but if desired the setting may be checked from time to time via S_3. The grid current taken by the thyratron from the working electrode is usually less than 1 microamp.

In use it is only necessary to set the desired potential upon the external potentiometer, and the potentiostat automatically adjusts the current to give this potential at the electrode. The current which passes is actually fluctuating slightly about a mean value, since it is tending continually to rise and being repeatedly prevented from doing so by the controller circuit, but these operations take place so rapidly that an ammeter in the circuit usually shows a substantially steady reading.

SECTION 3: PREPARATIONS

(*See* Vol. II, p. 371)

Potassium Bromate. 25 grams of potassium bromide and 0.2 gram of potassium chromate are dissolved in 100 ml. of water and the solution electrolysed between a platinum anode and a platinum or nickel cathode at 35–45°. The addition of the potassium chromate obviates the need for a porous diaphragm. The anodic and cathodic C.D.s should be approximately 0·1 amp./sq. cm. After current has been passed for about 25 amp.-hours, the solution is evaporated to 40 ml. when the potassium bromate crystallizes out. The current efficiency is greater than 90 per cent and the weight yield about 70 per cent of theory.

Cobaltic Sulphate. The anolyte consists of 24 grams of cobaltous sulphate ($CoSO_4.7H_2O$) in approximately 75 ml. of warm 8 N sulphuric acid and is contained in a porous pot; dilute sulphuric acid may be used as catholyte. A platinum foil anode and a copper cathode are employed, the anodic C.D. being approximately 0·02 amp./sq. cm.; the cathodic C.D. is immaterial. The electrolysis is started at a temperature of approximately 30° (in order to keep the cobaltous sulphate in solution), and as it proceeds the temperature is gradually lowered. After about 12 amp.-hours a thick mass of green needles of cobaltic sulphate ($Co_2(SO_4)_3.18H_2O$) separates out. The current efficiency is low.

Sodium Perchlorate. A concentrated solution of sodium chlorate containing 700 grams per litre is electrolysed in a cell without a diaphragm, between smooth platinum anodes and iron cathodes. A high current density is used, 0·3–0·5 amps. per sq. cm. This causes a rise of temperature which does not affect the oxidation efficiency up to 60°; the cells are therefore allowed to run hot. An 85 per cent oxidation to perchlorate is obtained by this method.

Sodium Arsenate. A solution containing about 80 grams of arsenious oxide and 100 grams of sodium hydroxide, per litre, is electrolysed between iron electrodes; at a current density of 0·033 amps. per sq. cm. the arsenite is oxidized to arsenate with the theoretical efficiency. Lime water is added to the resulting solution to precipitate the calcium arsenate.

Benzaldehyde. 20 grams toluene, 100 ml. of sulphuric acid (10 per cent) and 100 ml. of acetone constitute the cell—a vessel with stopper and filter with stirrer. Two anodes of sheet platinum are placed diametrically opposite to each other. Spirals of platinum wire are used for the two cathodes—placed between the anodes and near the sides of the containing vessel. Current density 1·8 amperes, E.M.F. 6 volts—for approx. 25 hours. The containing vessel is cooled in running water and the temperature kept below 20°. The mixture is well stirred during the reaction. The reaction mixture after the oxidation is neutralized, the acetone is distilled off and the benzaldehyde and residual toluene are then separated from the reaction mixture by steam distillation. The crude benzaldehyde is purified through its bisulphate compound. The weight of pure, redistilled benzaldehyde is about 25 to 30 per cent.

p-Nitrobenzyl Alcohol. 15 grams of *p*-nitrotoluene dissolved in a mixture of 80 grams of glacial acetic acid, 15 grams of sulphuric acid, and 7 grams of water is used as anolyte and is contained in a porous pot; the catholyte is sulphuric acid of specific gravity 1·6 to 1·7. A platinum foil anode and a lead cathode are employed. The anodic C.D. should be approximately 0·015 amp./sq. cm., while that at the cathode is immaterial. The electrolysis is carried out with the cell immersed in a boiling water bath, and about three times the theoretical quantity of electricity is passed. The dark brown anode liquid obtained is steam distilled to remove impurities and the mother liquor filtered. Any residue is extracted with boiling water and the washings added to the filtrate. *p*-nitrobenzyl alcohol crystallizes out from the filtrate on cooling, and may be recrystallized from hot water. The current efficiency is about 30 per cent and the weight yield about 40 per cent of theory.

CHAPTER XXI[3]

MISCELLANEOUS

SECTION 1 : LABORATORY TECHNIQUE

(*See* Vol. I, Chap. VIII)

THE Laboratory Workshop. Such operations as glass-blowing and laboratory manipulation and workshop practice generally, including silvering of glass, working of fused silica, mounting cross-wires in microscopes, erection of special apparatus, construction of resistance coils, use of thermionic valves, and workshop practice generally, require more than mere description for successful accomplishment. The ordinary operations of the physical-chemical laboratory are best considered in connexion with particular processes and experiments, and the various chapters should be consulted for particular points. There are a few items, however, which are of more general application, and are required under many headings. Many of these are considered in Vols. I and II.

The workshop itself is an important and indispensable consideration. It should, for preference, be situated on the ground floor and need not occupy very much space. It should contain at least a small vertical lathe, screw-cutting drill, carpenter's bench, a small hydraulic press, and various instrument-making tools. Such a workshop will be of great assistance and may save loss of time in repairs of apparatus and plant and in providing for new apparatus and equipment. For particulars of special texts on laboratory aids—*see* ' Guide to Further Reading ', Vol. I.

In this section some general equipment and a few points in laboratory technique will be briefly reviewed.

The Hot Stage Apparatus. The accurate determination of certain physical constants of micro-quantities with changes of temperature has been greatly facilitated by the technique of Kofler.[1] With minute crystals continuous observation of changes in the sample before, during and after melting can be observed. The technique is also useful in micro-preparation work, sublimation, incineration, measurement of refractive indices at high temperatures, fusions, heating under controlled conditions, &c. The A.H.T. apparatus[2] (Fig. 1 (XXI^3)), made to Kofler's specification, can be used for temperatures up to 350°, with an accuracy of ± 0·5° in the range to 200° and of ± 1·0° in higher range. It can also be used with transmitted, reflected or polarized light on any compound microscope providing magnifications from 50 to 100 × with objective having working distance of 6 mm. or more, and preferably with a metal stage.

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[1] Kofler, ' Mikroskopische Methoden zur Identifizierung Organischer Substanzen ', Beiheft 36, *Zeitschrift für Angewandte Chemie* (1940) ; *Mikrochemie*, 1934, *15*, 242 ; Kofler, Kofler and Maryhofer, *Mikroskopische Methoden in der Mikrochemie*, Vienna, 1936.

[2] Made by Arthur H. Thomas Co., Philadelphia, U.S.A.

The apparatus consists essentially of an insulated metal stage, 90 mm. diameter × 20 mm. high, A, heated by an embedded Nichrome unit, and with a central light well fitted with a condensing lens system. A threaded post takes either a fork for the micro-slide or various sublimation blocks. A vertical rheostat, specially designed for use with this Hot Stage, permits exact reproduction of settings. It is attached to lead R.

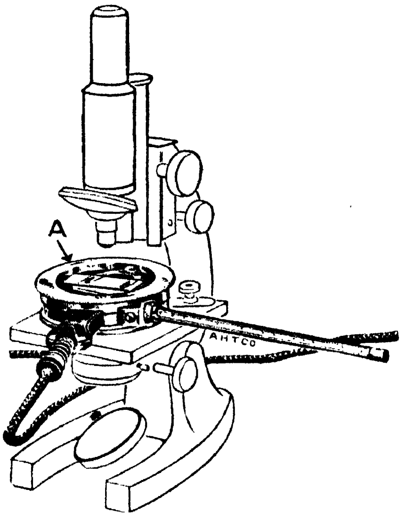

FIG. 1 (XXI^3)
The hot stage apparatus

The thermometers used are calibrated on the individual Hot Stage with which they are to be used. A set of eight stable test reagents is included with each outfit. They are convenient, not only in acquainting the user with manipulation of the instrument, but also for the preparation of a calibration chart for the rheostat.

Two adjustable arms with pin ends, which fit into holes provided for the microscope stage clips, permit attachment to the stage of the microscope and alignment within the optical axis of the microscope. The thermometers are prepared in the following manner: a blank thermometer of suitable size is inserted in the stage, fixed in a reproducible position by internal clips and protected by the metal guard as in actual use ; six points are then marked on the stem by making micro-melting-point determinations with selected stable substances of predetermined melting-point values, after which graduations in 1° divisions are engraved in the usual manner. Readings taken at the time of melting of unknown substances therefore correspond to temperatures prevailing on the micro-slide and represent corrected micro-melting-points which are generally accepted as a suitable physical constant for the identification of compounds. The two thermometers supplied with each Hot Stage have ranges from + 30 to 230° and + 60 to 350°, respectively.

Micro-incineration. The ashing of paraffin sections on slides can be carried out in a simple electric furnace tube. Details for such a method have been described by Gage ;[1] with his microscopic outfit it is possible to obtain the amount of inorganic substances in individual cells and in different parts of tissues and organs.

A Hot Stage apparatus suitable for the study of reactions over a wide range in temperature has been constructed by Wallace and Willard.[2] An

[1] *Stain Technol.* (Cornell Univ., Ithaca, N.Y.), 1938, *13*, 25.

[2] *Ind. Eng. Chem. Anal.*, 1929, *1*, 106.

improved design has been made by Vold and Doscher.[1] It is suitable for microscopic observations between laboratory temperature and 350°. The heated chamber in the improved design is 2·5 in. square and 0·75 in. high from which the central portion has been drilled leaving small terraces. A thin brass ring fits into a slot, thus creating an annular space into which is inserted a heating element. This is tightly wrapped around the brass ring and is separated from it by two strips of mica in order to prevent the development of hot spots. Two glass disks ($\frac{1}{16}$ in.) are separated by an air space asbestos spacer ($\frac{1}{32}$ in.), and fit into the well created by the brass ring, leaving approximately $\frac{1}{16}$ in. from the top of the ring to the top of the glass disk. These glass disks serve to insulate the heated air chamber of the furnace from the condenser system of the microscope, as well as prevent too great a heat loss from the centre of the main hot stage chamber. This is an effective technique, since the lower chamber is heated by the brass ring almost as effectively as is the upper chamber. The microscope objective is protected from the furnace by a Pyrex disk. The latter condition is important if the furnace is to be used with a polarizing microscope, in order to prevent depolarization by the disk. The 0·125 in. disk is used rather than another dummy air space, as formed on the underside of the main hot stage chamber, because of its greater convenience when changing specimens. A small hole ($\frac{1}{64}$ in.) drilled through the block and the brass ring permitted the entrance of a thermocouple for measuring the temperature within the ring. Copper-constantan thermocouple wire, No. 30. B. & S. gauge, was used. Since the e.m.f. is 0·04 to 0·05 mv. per degree Centigrade, a Leeds and Northrup potentiometer and galvanometer, with a sensitivity of 0·015 microampere per mm., was satisfactory. The original paper should be consulted for working details.[2]

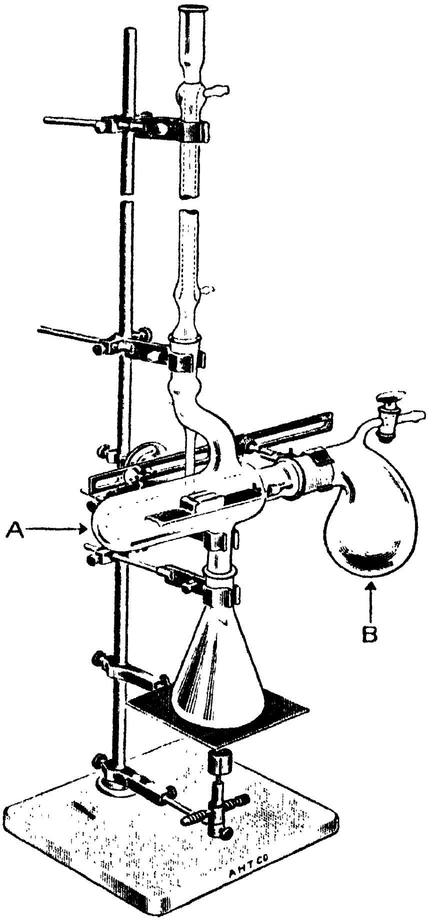

FIG. 2 (XXI[3])
The Abderhalden vacuum drying apparatus

Vacuum Drying Apparatus (*see* Vol. I, p. 199). This Abderhalden model[3] is shown in Fig. 2 (XXIV[3]). It provides for drying over prolonged periods at constant temperatures at reduced pressure without accessory mechanical temperature control devices. The A.H.T. apparatus [1] (Fig. 2 (XXI^3)) consists of a drying apparatus of Pyrex glass with drying chamber A, approximately 250 mm. long × 26 mm. minimum inside diameter, with by-pass, and connected by ground joint with pistol-shaped desiccant chamber B ; complete with reflux condenser of Pyrex glass and Erlenmeyer flask, 300 ml. capacity, with interchangeable joints throughout ; mounted on a support with special spring-grip clamps and micro-burner.

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[1] *Ibid.*, 1946, *18*, 154.

[2] *Loc. cit.*

[3] Manufactured by Arthur H. Thomas Co., Philadelphia, U.S.A.

The by-pass for condensate results in greater temperature uniformity than was possible in the original execution. Temperature range is limited only by the number and variety of constant boiling liquids which are available.

The use of the spring-grip clamp mounted on slotted bar with adjustable holder permits detachment and support of the desiccant chamber in mid-air, thereby offering the advantages of convenient filling and refilling of the chamber, of avoiding damage from scratching or breakage which might result from placing it on the work table, and of undisturbed access to the drying-chamber for delicate manipulations. Dehydrite, Drierite or Anhydrone are suggested for use in the desiccant chamber.[2]

Vacuum Sublimation. A brief reference has been made in Vol. II (p. 134) to Hibben's sublimation technique.[3] This process is of importance for the removal of dissolved gases from a liquid in the final step in the purification of a liquid for the purpose of determining certain of its physical properties. Removal by chemical means is often impracticable, particularly in the case of the gases of the atmosphere. The collection of the dissolved gas for analytical purposes is also of importance, for example, in determinations of gas solubilities. The purification not only permits the complete removal of the dissolved gas, in most cases, but also allows an approximately complete recovery of both the gas and liquid.

The various methods described in the literature fall into four categories—those employing vacuum,[4] those employing heat,[5] those employing both vacuum and heat,[6] and those employing freezing.[7] The vacuum sublimation process includes all the processes named above, since it employs heat, vacuum, and freezing.

The conditions, according to Hibben, essential to the best operation of the process of purification by vacuum sublimation are as follows : (*a*) The temperature at the condensing surface must be considerably below the freezing-point of the pure liquid so that its vapour condenses directly to a solid, otherwise a solution of the gas impurity may occur again if a liquid phase is present at the condensing surface during condensation. (*b*) The sublimate must have a negligible vapour pressure at the temperature of condensation or a loss of the pure material will result. (*c*) The third condition can be stated in the following general form : The vapour pressure of the impurity from any system containing it which can exist on the condenser must be greater than the partial pressure of the impurity in the gas phase.

---

[1] *See* ref. 3, p. 580.

[2] *See* Alber, ' Hygroscopic Substances in Microanalysis ', *Mikrochemie vereinigt mit Mikrochimica Acta,* 1938, Band XXV, Heft 1–4, 47.

[3] *Bureau of Standards J. of Res.,* 1929, *3,* 97.

[4] *See* Hibben's paper (*loc. cit.*) for references.

[5] Reichardt, *Z. anal. Chem.,* 1872, *11,* 271 ; Jacobsen, *Ann.,* 1873, *167,* 12 ; Petterson, *Ber.,* 1889, *22,* 1434.

[6] Lorah, Williams, and Thompson, *J. Amer. Chem. Soc.,* 1927, *49,* 2991.

[7] Faraday, *Research in Chemistry and Physics,* Taylor and Francis, 1859, p. 373.

The original paper should be consulted for details of his apparatus and its working.

Sublimation in High Vacuo.[1] This type of sublimation may be obtained by heating in the vacuum of the cathode ray.[2] Under such conditions the following sublimation points have been determined :

Anthracene	103°–104°	Salicylic acid	75°–76°
Phenanthrene	95°–96°	Camphoric acid	163°–164°
Chrysene	109°	Theobromine	156°
Pyrogallol	105°–106°	Antipyrine	141°–142°
Caffeine	116°	Indigo	156°–158°
Alizarin	153°–155°	Carbamide	125°
Retene	135°	Thiocarbamide	98°–99°

The sublimation point of an organic substance is often a definite characteristic of the compound. According to Allen[3] the method of A. Wynter Blyth is recommended when a dependable and comparable value is required. The sublimation point is the lowest temperature which, if maintained for 60 seconds, allows of the formation of a trace of sublimate visible to a microscopic power of 0·25 in.

The Air Drying of Solid Materials (*see* Vol. I, p. 199)

In the method of drying by hot air the consumption of heat is comparatively large. This is due to the high latent heat of evaporation and the difficulties attending the economical utilization of waste heat. Air drying is employed when other methods (e.g. draining, pressing) are impracticable. A review of this method has been made by Tassie.[4]

Hygroscopic Moisture Content. The moisture content of a material in equilibrium with the relative humidity of the surrounding atmosphere is termed its hygroscopic or equilibrium water content or ‘ regain ’. It varies at constant humidity, widely with different materials, and slightly with temperature for a given material. A knowledge of this value is of importance in determining the conditions at the end of a drying process, and for estimating the amount of moisture acquired from the atmosphere during storage. It is especially important that wood should be installed at a moisture content in accordance with its service conditions, to minimize changes in size or distortion of section. Here also a knowledge of hygroscopic moisture content at different relative humidities is of great assistance.

Hygroscopic moisture is determined by exposing two samples of a given material to a current of air at constant relative humidity and temperature until no further change in weight occurs. The moisture contents are then determined in the usual manner, and are returned as parts of water per hundred parts of dry material. The moisture content of one of the samples must be less, that of the other greater, than the hygroscopic moisture content of the material. This is taken to be the average value for the two tests.

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[1] *Thorpe's Dictionary of Applied Chemistry*, 3rd ed. Article on ‘Sublimation’ by Reilly.

[2] Krafft and Wielandt, *Ber.*, 1896, *29*, 1316, 2240.

[3] Commercial Organic Analysis, 5th ed., Vol. I, p. 18.

[4] Private communication.

In the same material the hygroscopic moisture content often varies greatly and is dependent upon the prior history of the material.

Importance of Controlled Drying. Certain materials (e.g. wood) shrink as they dry. In drying wood it is essential to avoid too rapid evaporation of water, since the surface becomes dry and shrinks, while the incompressible interior is still wet. This results in the production of cracks or 'checks'. It is therefore necessary to use air of such a humidity that evaporation keeps pace with the internal diffusion of water.

'Case hardening' (e.g. in the drying of cordite) is due to the formation of a dry surface layer relatively impervious to water and is caused by an excessive difference between the solvent contents of the surface and of the interior of the material. It can sometimes be remedied by controlled humidity drying, with a consequent reduction in the time required.

Often when drying sheet materials the edges dry far more rapidly than the middle. Owing to unequal shrinkage, the materials warp. If the sheets are supported on frames in such a manner that the edges are protected, drying takes place uniformly, and warping is thereby eliminated.

Mechanism of Drying Processes. As long as the surface of a solid is wet the rate of evaporation under given conditions is constant over a range of moisture contents for certain materials. It is held that over this range, the *constant-rate period*, water is fed to the surface by capillarity. Soon the surface of the solid appears dry and the rate of drying decreases. This part of the process is known as the *falling-rate period.* The moisture content at the end of the constant-rate period and the beginning of the latter period is termed the *critical moisture content.*

The critical moisture content varies for different materials, and for a given material differs slightly with the rate of drying and with the initial moisture content.

At the hygroscopic moisture content corresponding to the prevailing conditions of temperature and humidity the rate of drying obviously becomes zero.

Constant-rate Period. During this period the rate of drying depends upon the difference between the vapour pressure of water at the temperature of the solid and the partial pressure of the atmospheric water vapour and for most purposes may be assumed proportional to this difference. It also depends upon the air velocity and is inversely proportional to the average partial pressure of air in the surface film.[1]

Theoretically, the solid should assure the temperature shown by a wet bulb thermometer placed in the air stream. In practice, however, owing to the reception of heat by radiation, or by conduction from nearby dry surfaces of the solid, the temperature is usually somewhat higher. Also the rate of evaporation is greater than the value calculated on the assumption that the pressure of the water vapour is identical with that corresponding to the wet bulb temperature. The effect of radiation may be calculated, but it is difficult to make an allowance for heat conduction.[2]

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[1] *Ind. Eng. Chem.*, 1934, *26*, 516.

[2] *Ibid.*, 1929, *21*, 976.

Towards the end of the constant-rate period it is not possible to determine with certainty, by inspection, whether or not surface evaporation is taking place. A test has been developed for this purpose.[1]

Falling-rate Period. During this period the rate of drying may be determined by the resistance to the removal of water vapour or to water movement within the solid. Discontinuities in the drying curves (i.e. rate of drying versus water content) indicate where the mechanism changes.

With close-textured materials (e.g. clay) surface evaporation continues until low moisture contents are reached, owing to the ease with which water movement can take place. With materials of loose structure the rate of water transfer is not sufficiently great, so that under-surface evaporation takes place.

Drying Curves. According to Sherwood [2] the types of curves shown in Fig. 3 (XXI^{3}), *a*, *b*, *c*, and *d*, are commonly obtained.

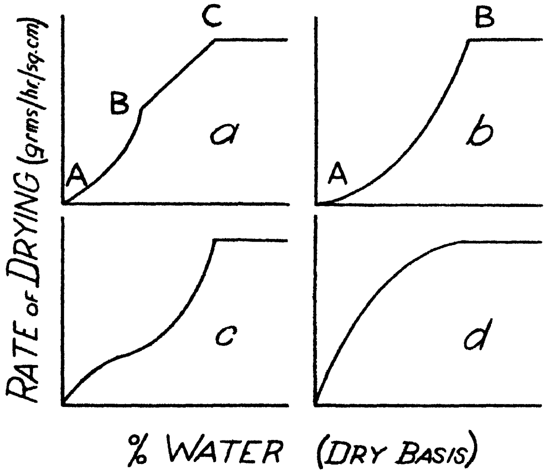

FIG. 3 (XXI^{3})
Rate of drying curves—4 types

Types a and b. Internal diffusion may be expected in the portion designated AB. Here the rate of drying will depend on temperature, on the thickness of the material, and on humidity in so far as humidity influences the equilibrium moisture content. The rate of drying will be independent of air velocity. In the portion BC the rate will be determined by the removal of vapour from the surface. With materials where internal diffusion controls throughout the falling-rate period a constant-rate period is not usually obtained. The first type of curve is obtained with porous ceramic plates, powdered calcium carbonate, &c., while the second is obtained with soap and wood.

Type c. This is typical of solids into which the zone of evaporation retreats during the drying process. In the early stages of the falling-rate period the rate of evaporation is controlled by vapour removal from the surface. Consequently the factors affecting the rate of drying are the same as those operating during the constant-rate period. As dryness is approached, the rate of drying is determined by the rate of vapour transfer through the solid. Curves of this type are obtained for the drying of pulp, and of crude sodium chloride (Rock salt) contained in a galvanized iron tray.

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[1] *Loc. cit.*

[2] *Trans. Chem. Engineering Congress of World's Power Conference*, London, 1936, 2, 346–63, Lund Humphries & Co., Ltd., London.

Type d. Here the rate of drying is determined by the removal of vapour from the surface of the material. This is typical of cellulosic material such as paper.

Equations for Solution of Problems on Drying. (*a*) The following equation[1] is recommended for estimating the rate of evaporation for air velocities of 1·5 to 7 metres per second at approximately 20° C.

$$W = 0{\cdot}027\, V^{0{\cdot}8}\,(P_w - P_a) \quad . \quad . \quad . \quad . \quad \text{(i)}$$

Here, W = rate of evaporation (kg. per sq. m. per hour)
V = velocity of parallel air stream over surface (m. per sec.)
P_w = vapour pressure at temp. of solid (mm. mercury)
P_a = partial pressure of atmospheric water vapour (mm. mercury).

(*b*) The rate of drying in the falling-rate period is assumed to be proportional to the free water content $(T - T_e)$

$$\text{i.e. } \frac{dT}{d\theta} = -k(T - T_e)$$

or

$$\log_e \frac{T_o - T_e}{T - T_e} = k\theta_f \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

The rate of drying during the constant-rate period is the same as at the critical moisture content.

$$\text{Hence, } \frac{dT}{d\theta} = -k(T_c - T_e)$$

$$\therefore \theta_c = \frac{T_o - T_c}{k(T_c - T_e)} \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

Here, T = water content at a time θ after start of period considered
T_e = equilibrium moisture content corresponding to prevailing humidity (dry basis)
T_c and T_o = critical and initial, moisture contents respectively (dry basis)
θ_c and θ_f = time of drying during the constant-rate and falling-rate periods respectively
k = constant.

(*c*) Since the rate of drying during the constant-rate period is:

$$k(T_c - T_e)\frac{w}{A} = W \ (\textit{see} \text{ equation (i)})$$

the constant k may be evaluated.

Here, w = weight of dry solid (*kg.*)
A = wetted surface of solid (sq. m.).

Drying by Sublimation.[2] This process is composed of three stages

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[1] *Trans. Chem. Engineering Congress of World's Power Conference*, London, 1936, *2*, 346–63, Lund Humphries & Co., Ltd., London.

[2] *Ind. Chemist*, 1945, *21*, 466.

(1) freezing of the product; (2) sublimation of the ice thus produced, under very low pressure; (3) removal of residual water at a higher temperature (up to 70° C). With a suitable vacuum and by rapid application of heat the process can be made industrially workable. Water vapour is removed (*a*) by condensation using suitable refrigerants; (*b*) by means of desiccating agents (laboratory method); or (*c*) direct pumping of the water vapour. This is the simplest commercial method.

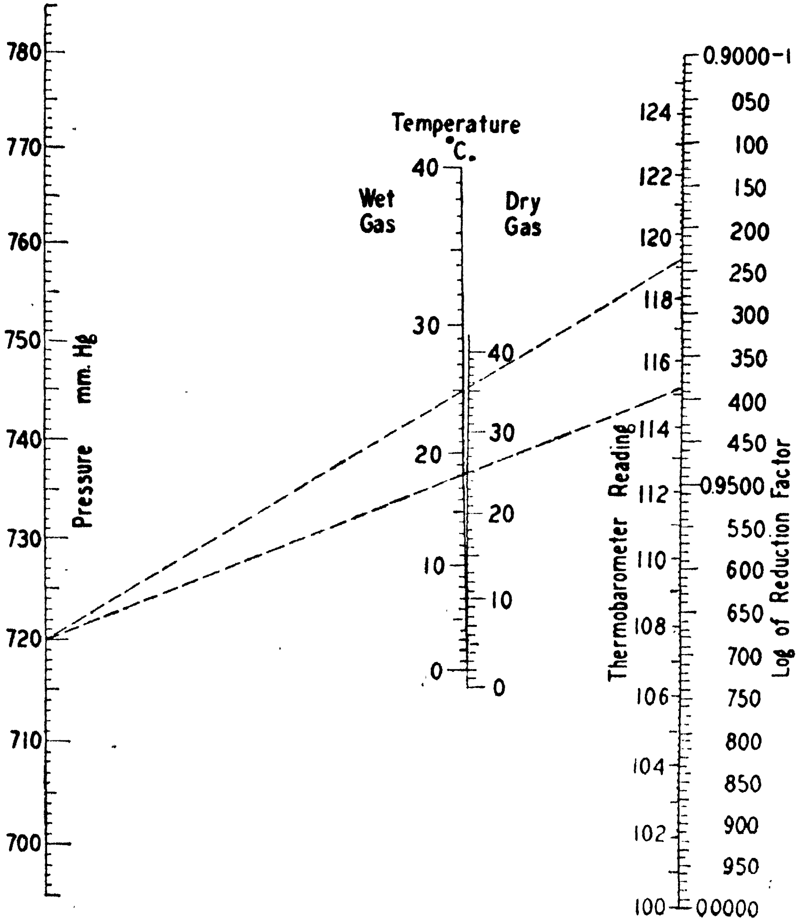

FIG. 4 (XXI³)
Nomograph for use with the thermobarometer

The advantages claimed for this process are as follows: (1) Many labile substances are stable at the low temperatures used; (2) minimum loss of volatile components; (3) elimination of foaming and case hardening; (4) protection from oxidation; (5) increased rate of solution of the dried products.

Oil Flotation. The following method has been employed to render wet aggregates fit for use with, for example, tar materials. Paraffin oil is poured over the material. Owing to the difference in surface tension between the two liquids the water is rapidly displaced and flows out at the bottom of the pile.

Electro-drying. This process is suitable for peat, ball clay, and china clay. The wet material is placed between two conducting surfaces. On passing direct current through the mass the water is rejected by endosmosis. The water content of peat may in a few minutes be reduced from 93 per cent to about 45 per cent, and that of clay to about 20 to 28 per cent in the same time.

When treating china clay a small amount of a peptizing electrolyte, e.g. sodium carbonate, is added—approximately 0·01 per cent on the weight of the dry clay. This is adsorbed on the faces of the particles. The clay is peptized, and its particles are rendered capable of movement in the electric field. Impurities such as very finely divided iron pyrites do not adsorb the electrolyte and are incapable of such movement. This method has been used on a large scale for drying and at the same time purifying china clay. It has proved itself most economical for this purpose, removing impurities that could not be eliminated by other means.

Thermobarometer. This apparatus has been designed to assist in the rapid correction of gas volumes obtained in gas analytical determination to normal temperature and pressure. A nomograph, Fig. 4 (XXI^3), somewhat similar in principle to that of Farmer, is used in correlating gas volumes under different conditions[1] (*see* Vol. I, p. 152).

A known volume of air expands or contracts with the continuous changes in atmospheric pressure and temperature of the room in which the gas determinations are carried out. If the air in the thermobarometer and the analysis gas are in equilibrium with the atmospheric pressure and at the same temperature, the volume occupied by the air is substituted in Equation 1 as thermobarometer reading. The necessity for equality in temperature requires that gases evolved in exothermic analytical reactions be allowed sufficient time to return to room temperature. In contrast to the well-known Lunge or Hempel compensator, only one thermobarometer is necessary for an entire battery of gas burettes using identical confining liquids.

In the equation :

$$A = \frac{V \times f \times 10}{\text{T.R.} \times W} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$\log A = \log V + \log \text{R.F.} + \log f + 1 - \log W \quad . \quad . \quad (2)$$

A = weight per cent of constituent Y to be determined analytically
V = gas volume measured at room temperature and prevailing atmospheric pressure.
f = conversion factor of gas volume into weight of desired constituent (*see* 18).
T.R. = thermobarometer reading at room temperature and prevailing atmospheric pressure.
W = weight of sample in grams.

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[1] Berl, Berl and Sterbutzel, *Ind. Eng. Chem. Anal.*, **1945**, *17*, **166**.

log R.F. = log of reduction factor from Fig. 4 (XXI[3]) for a given thermobarometer reading.

The thermobarometer Fig. 5 (XXI[3]) is drawn to scale. It consists of tube A with stop-cock 1 with an upper uncalibrated part of 90 ml. volume and the lower calibrated part of 35 ml. volume subdivided into scale divisions of 0·05 ml. and numbered at each ml. Tube B, open to the atmosphere, is placed as near as possible to tube A, having identical though unnumbered calibration marks. Levelling bulb C is connected with heavy rubber tubing to A and B through stop-cock 2. Whenever a thermobarometer reading is to be made, the mercury levels in A and B are equalized by opening stop-cock 2 with levelling bulb C in position to receive from or add mercury to tubes A and B. When the mercury levels in A and B are identical, stop-cock 2 is closed and the volume reading is substituted in Equation 1.

To adjust the thermobarometer initially, temperature and barometric pressure in the laboratory are determined. Assume that a temperature of 25° and a barometric pressure of 720 mm. of mercury exist at the time of adjustment. If dry gases—for instance, nitric oxide in the Lunge nitrometer over mercury—are being measured, 720·0 (pressure scale) is connected with 25·0 (temperature scale, dry gas) or the nomograph and extended to thermobarometer reading scale. This scale indicates that 100 ml. of dry air at N.T.P. expand to 115·21 ml. at the prevailing pressure and temperature. Air dried with a drying agent, such as phosphorus pentoxide, calcium chloride, &c., is introduced into the dry tube, A, which was initially filled with mercury. Stop-cock 1 is closed permanently when the mercury in tubes A and B are level at a scale reading of 115·21.

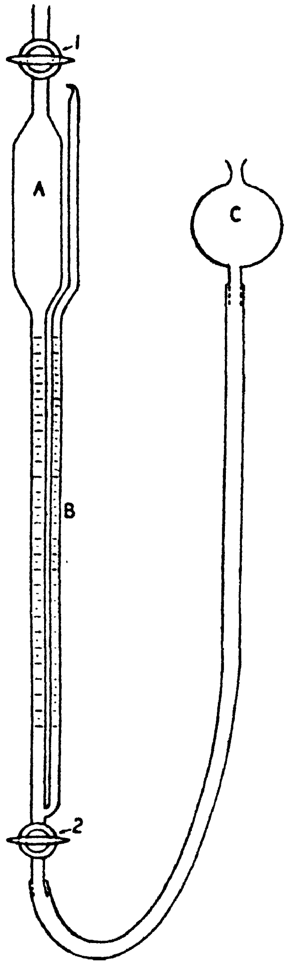

FIG. 5 (XXI[3])
The thermobarometer

A Gas-Specific-Gravity Balance. An apparatus for the accurate and rapid determination of the specific gravities of gases in large or small quantities, depending on the counterbalancing by riders of the change in upthrust on a glass bulb when surrounded by air and gas. It has been described by Hales and Moss.[1, 2] A high degree of damping allows high sensitivity to be employed without loss of speed. Comparison tests show that it is accurate to one or two in the third decimal place over the range from hydrogen to carbon dioxide.

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[1] *J. Sci. Inst.*, 1935, *12*, 309.

[2] Prov. Pat. No. 14196/35.

The apparatus is:

(1) Suitable for any gas, including hydrogen, and soluble gases.
(2) Suitable for small quantities of gas.
(3) Portable and self-contained.
(4) Inexpensive and simple in construction.
(5) More rapid in operation than existing types.
(6) At least as accurate as the best of the existing instruments.

These features are embodied in the instrument of Hales and Moss, and tests have shown it to be accurate, and easy and rapid to manipulate. The essential details of the instrument [1] are shown in Fig. 6 (XXI³). A sealed glass bulb A is fixed to the short end of a long pivoted beam B which has an adjustable counterpoise C, the pivot D being an agate knife-edge; this bulb is enclosed in a fixed spherical bulb E, which is composed of two glass hemispheres joined by a gastight clip. In order to avoid errors due to the different coefficients of expansion of glass and metal, the beam is continued into the centre of the bulb A, being fixed there by sealing wax to the inner end of a glass tube which is sealed in the bulb A. The beam B is divided into ten equal parts by notches. Two riders M and N are provided for the measurement of the specific gravity, N being one-tenth of the weight of M. A third rider L, equal in weight to the smaller rider N, slides on a rail attached to the underside of the beam, and is used in determining the gas factor, that is, the factor by which a volume of gas must be multiplied to reduce it to standard temperature and pressure. A scale F indicates the position of the beam. A constriction J bypasses the cock G on the inlet to the space between bulbs A and E, and serves as a small leak to prevent back diffusion of air through the outlet H. P is a tube containing calcium chloride for drying the gases to avoid inaccuracies due to unknown degrees of saturation.

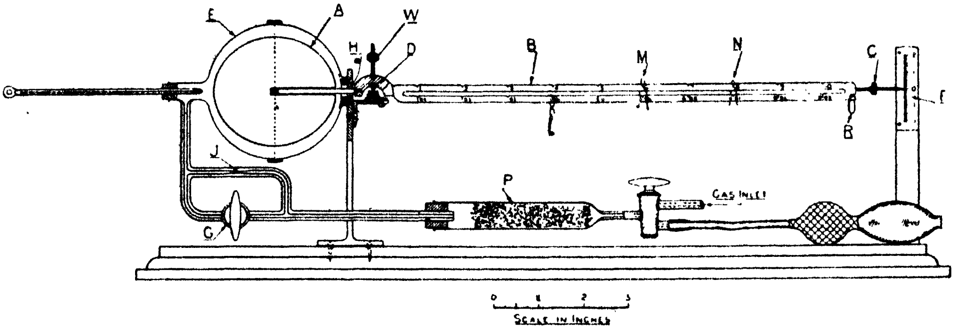

FIG. 6 (XXI³)
A gas-specific-gravity balance

The accompanying table [2] contains the results of a number of tests on gases of widely different specific gravities made with the new instrument in comparison with (*a*) an effusion type instrument and (*b*) the balanced columns method using a Chattock gauge as micromanometer.[1]

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[1] Manufacturers: Griffin & Tatlock, Kingsway, London.
[2] *J. Sci. Inst.*, 1935, *12*, 309.

TABLE OF EXPERIMENTAL RESULTS

Gas	Effusion bell sp. gr. = $(t_1/t_2)^2$ (saturated) * Dry specific gravity	Balanced columns sp. gr. = $1 - Kd/f$ (dry) Dry specific gravity	Hale and Moss' apparatus sp. gr. = $1 - d/f$ (dry) Dry specific gravity
Hydrogen (cylinder) . . .	0·080	0·078	0·077
Residual gas, hydrogenation expt.	Insufficient gas	0·088	0·087
,, ,, ,,	,, ,,	0·110	0·109
,, ,, ,,	,, ,,	0·292	0·294
Coal gas	0·346	0·345	0·343
,, ,, ...	0·360	0·353	0·351
,, ,, ...	0·388	0·377	0·379
,, ,, ...	0·406	0·402	0·400
Dissolved gas, hydrogenation expt.	Insufficient gas	0·488	0·485
,, ,, ,,	,, ,,	0·595	0·597
Oxygen (cylinder)	1·111	1·107	1·108
Carbon dioxide (cylinder) . .	1·454	1·524	1·528

* Saturation assumed, but probably not, complete.

Micro-balance. A simple quartz torsion balance with a capacity of 50 to 100 mg. and a sensitivity of ± 0·1 has been described by Lowry.[2] The balance is shown in outline in Fig. 7 (XXI[3]). The beam A consists of a hollow quartz tube 25 cm. in length and about 1 mm. in diameter. This tube is suspended in a quartz yoke B between two horizontal quartz fibres C.

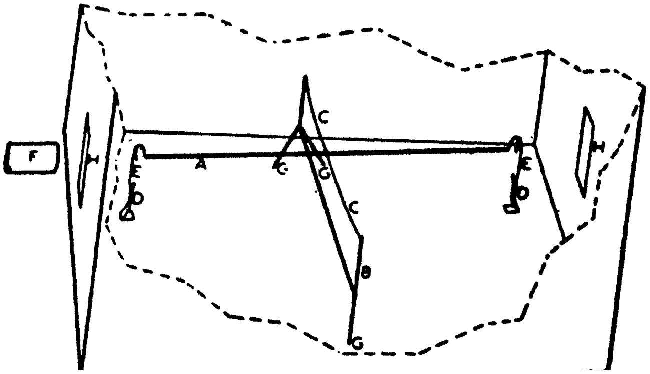

FIG. 7 (XXI[3])
A quartz torsion balance—shown in outline

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[1] Blackie, A., *Fuel Research Technical Paper No. 5.*

[2] *J. Biol. Chem.*, 1944, *152*, 293 ; *cf. also* Barrett, Best and Ridout, *J. Physiol.*, 1938, *93*, 367.

The pans D which are made of aluminium foil are suspended from quartz hooks E which in turn are suspended from fine quartz loops in the ends of the beam. No attempt was made to make the two halves of the beam of exactly equal length.

Unequal loading of the beam causes a displacement which is opposed by the resultant torsion in the quartz fibres. The displacement of one end of the beam is measured with cathetometer F reading to ± 0·01 mm. This displacement is proportionate to the weight added to the pan. In the balance described a displacement of 1·00 mm. is equivalent to 10·87 units.

Automatic Siphon. An automatic siphon, useful for siphoning liquids where sucking to start the flow is impossible or inconvenient, is described by Tompa.[1] It consists of a bent tube whose shorter limb is surrounded by a bulb with a constricted opening ; the bulb communicates with the tube by a small hole at the top (Fig. 8 (XXI[3])). If the shorter limb is plunged into a liquid so that the bulb is fully immersed and the bend is not too high above the surface, liquid rises at once up the inner tube and slowly into the bulb : it pushes the air there through the hole into the tube, where it rises and, acting as an air lift, carries the liquid over the top of the bend. Once started, the siphon acts as an ordinary siphon. The dimensions given in the sketch have been found satisfactory, though they are probably not an optimum. The apparatus is simple to construct ; it is important to keep the opening at the mouth of the bulb small, so that it takes 3 to 5 seconds to expel the air.

Messrs. Kodak Ltd. have already marketed various models of automatic siphons of the above type.[2]

Calibration of Irregular-shaped Apparatus. The method consists in filling the vessel with carbon dioxide gas to a known pressure and then determining the weight of this gas after absorption by means of sodium hydroxide contained in asbestos. The method was worked out with a detailed example by Barkas and Paton.[3] Their procedure is as follows :

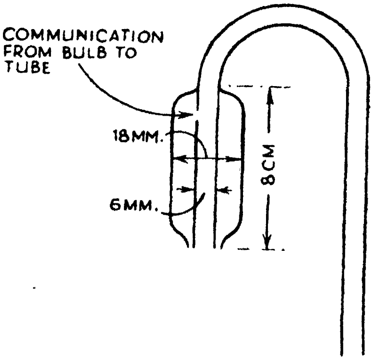

FIG. 8 (XXI[3])
An automatic siphon

The apparatus, kept at a constant temperature, is evacuated and filled with carbon dioxide to a known pressure less than atmospheric. The carbon dioxide from each volume is then allowed access to two previously evacuated and tared vessels containing soda asbestos and phosphorus pentoxide respectively. The carbon dioxide is absorbed by the soda asbestos according to the equation

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

The water set free during the reaction is absorbed by the phosphorus pentoxide. The volumes under determination varied from 100 ml. to 200 ml., and with these 1 hour is sufficient for almost complete absorption. At the end of this time the absorption vessels are closed, the pressure of the residual carbon dioxide is measured and the absorption vessels removed and weighed. From the data obtained, and taking 1·977 g./l, at N.T.P. as the accepted value for the density of carbon dioxide, the required volumes are calculated. If the final pressure is not zero a correction can be applied to allow for the expansion of the residual gas into dead spaces.

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[1] *J. Sci. Inst.*, 1944, *21*, 88. [2] *Ibid*, 1944, *21*, 128. [3] *Ibid.*, 1943, *20*, 163.

Let W_1 = the sum of the initial weights of absorption vessels in grams
W_2 = the sum of the final weights of absorption vessels in grams
P_1 = the initial measured pressure in centimetres of mercury
P_2 = the final measured pressure in centimetres of mercury
V = the required volume in millilitres
V_a = first approximation to required volume in millilitres
T = temperature in degrees Centigrade

$$V_a = \frac{W_2 - W_1}{1{\cdot}977} \times \frac{273 + T}{273} \times \frac{76}{P_1 - P_2} \times 1000$$

But the residual gas has expanded from V into the dead spaces V_d and the correct value for V is given by

$$V = \frac{W_2 - W_1}{1{\cdot}977} \times \frac{273 + T}{273} \times \frac{76}{P_1 - P_2[(V_a + V_d)/V_a]} \times 1000$$

In the more usual gas-expansion method the accuracy of the result varies with the ratio of the volumes of the known and unknown vessels, whereas in the method of Barkas and Paton the absolute accuracy is the same whatever the volume, depending only on the initial and final pressures of the carbon dioxide and the accuracy of weighing.

Galvanometer. Moving-coil galvanometers are nowadays chiefly used for the electrical measurements of temperature. They are classified according to the reading equipment into mirror and pointer galvanometers. Special modern constructions use direct beam or multiflex mirror indicators (e.g. Cambridge Spot galvanometer, B. Lange's—Berlin Multiflex Galvanometer) which combine in a very convenient and handy way the advantages of the mirror and pointer galvanometers for eye observations and/or photographic record.

The sensitivity of a moving-coil galvanometer (the relationship between current I and deviation angle α or $tg\,\alpha$ in case of greater deviations) is

$$I = \frac{D}{H.f.} . \alpha$$

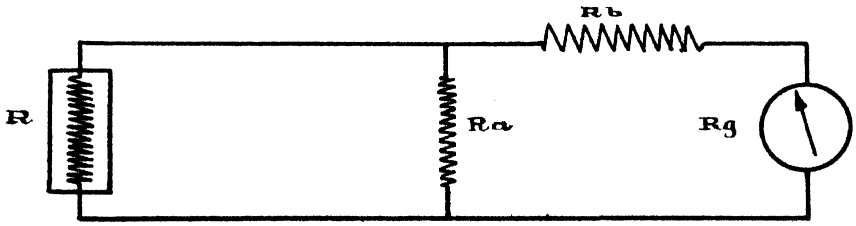
where D = direction force of the magnet on the coil
H = intensity of the magnetic field at the place of the coil
f = area of the coil.

The movement of the coil depends on the total resistance of the circuit in which the galvanometer is used. If the external resistance is high, then the galvanometer reaches its final position after a series of oscillations round this final position. In the case of a completely undamped system the oscillation period is

$$\tau = \pi \sqrt{\frac{J}{D}}$$

J being the moment of inertia of the coil. With decreasing resistance in the circuit the damping of the oscillations and their duration increase. For a certain resistance R the so-called critical damping (damping of the oscillations infinite) is reached. In this limiting case the galvanometer pointer reaches its final position in the shortest time without oscillations and $R = \frac{H.f^2.}{2\sqrt{J.D}}$. A further decrease of the external resistance produces 'creeping' of the pointer.

The external resistance to give critical damping, i.e. the limiting case in which the galvanometer oscillates periodically, is supplied by the maker. This critical damping has to be taken into consideration when using the galvanometer or when changing the sensitivity by introducing resistance (in parallel or in series).—Let R_g be the internal resistance of the galvanometer with the critical resistance R_G, R is the external resistance (e.g. thermocouple). If we intend to decrease the sensitivity of the galvanometer to $\frac{1}{m}$ of the original sensitivity by inserting a resistance R_a parallel and R_b in series to the galvanometer according to the following circuit (Fig. 8 (*a*)).



FIG· 8 (*a*).

then the most appropriate resistances R_a and R_b are those computed from the following two equations:

$$\frac{1}{\frac{1}{R_a} + \frac{1}{R}} + R_b = R_G$$

$$\frac{R_a}{R_b + R_g} = \frac{1}{m}$$

In the following table we have collected features of some galvanometers. Figures for instruments which are determined for highest sensitivity are not given and we have restricted the list to instruments which are used regularly in modern laboratories. The selection does not give preference to any particular manufacturer and is intended only to draw the attention to special constructions which proved to be of great value. The manufacturers will usually supply reliable advice as to the most suitable instrument for any particular purpose.

FEATURES OF SOME GALVANOMETERS FOR D.C. MEASUREMENTS

Type	Time of indication in seconds	Sensitivity	Internal resistance in ohms	Notes
Original Moll-*Mirror* galvanometer	1·3	105–57.10^{-10} amp. for 1 mm. deflection at 1 meter scale distance	55	Special mounting of coil (stretched between two wires or strips). Zero steadiness.
ditto	3·5, 7	0·2–8.10^{-10} *ditto*	340	*ditto*
Original Moll-*Mirror* Micro-galvanometer	0·2	250–400.10^{-10} *ditto*	20	*ditto*
Cambridge Spot-galvanometer	2·5	19–170 mm. on scale per micro-amp. (= readings taken to 0·2 mm. 10^{-8}–1·2.10^{-9})	10–700	Self-contained metal case comprising a reflecting galvanometer, a lamp, and a scale; robust construction, stable zero, accurate levelling unnecessary—portable.
B. Lange's Multiflex galvanometer	1–2 0·1	2.10^{-8}–2.10^{-9} amp. per division of 1 mm. length 10^{-6} amp. per division	60–5,000	Self-contained wooden case (23 × 19 × 24 cm.), weight 3 kg., comprising a mirror galvanometer with light pointer of 1 m. length in quadruple reflection, stretch band-system accurate levelling unnecessary, no bearing friction, very robust. Setting of light indicator with or without fine screw; arbitrary zero setting. Inter-changeable scales of 200 mm. length (1 division = 1 mm.) and switch for several ranges. Photographic recording equipment interchangeable with eye reading. Easily carried.
Zeiss' Loop-galvanometer	1	10^{-6}–10^{-10} amp. per division	10	Reading with microscope.
Pointer	12	10^{-7}–10^{-8} amp. per division	70–1,000	Metal ribbon suspension in small tower. Levelling necessary. Scale provided with mirror.
Galvanometer	7	3.10^{-7} and less amp. per division	10–1,000	Pivoted coil, robust; portable. Scale provided with mirror sometimes.

The Technique of Calibrating Platinum Thermocouples.[1] The use of the 'quick-immersion technique' for the measurement of liquid steel temperatures using a platinum, 13 per cent rhodium-platinum thermocouple made it desirable to have a standard calibration table for this type of thermometer over the range 1,400° to 1,770°. Such a table has been provided by the National Physical Laboratory and is given below:

E.M.F.–Temperature calibration of platinum, 13 per cent. Rhodium-platinum thermocouples over the range 1,400° to 1,770°, with cold junctions at 0°.

The E.M.F. values are given to the nearest 0·01 millivolt, but the absolute accuracy is not claimed to be better than ± 3° up to 1,600° and ± 5° above this temperature.

Temperature	1,400° millivolts	1,500° millivolts	1,600° millivolts	1,700° millivolts
0	16·00	17·43	18·81	20·16
10	16·15	17·57	18·95	20·29
20	16·29	17·71	19·08	20·42
30	16·43	17·85	19·22	20·55
40	16·58	17·98	19·35	20·68
50	16·72	18·12	19·49	20·81
60	16·86	18·26	19·62	20·94
70	17·00	18·40	19·76	21·07
80	17·14	18·54	19·89	—
90	17·29	18·67	20·02	—

Note. When compensating leads are used, care should be taken to ensure that the two junctions of the leads and thermocouple are at the same temperature and that this temperature does not exceed 100°. Otherwise, serious errors may be introduced.

Since individual couples may show small variations from the figures given and because after use for a number of determinations the E.M.F. given by a couple may fall, it is necessary to check them from time to time. It is recommended that they be checked at the palladium point (1,555°) and if any appreciable deviation from the standard value of the E.M.F. is found here to carry out a further check at the platinum point (1,773°).

Furnace. A furnace which is suitable for these determinations has a central tube of sintered alumina (Morgan R.R. or Thermal Syndicate), 300 mm. long, 12 mm. internal diameter, and 2·7 mm. thick. The lagging consists of pure alumina next to the winding on the tube and sil-o-cel powder or other suitable heat insulating material in the outer enclosure. It is most important that only pure alumina should be in contact with the main tube. The diameter of the outer case is 250 mm. for the lower temperature and the winding is 10 per cent rhodium-platinum foil, 12·5 mm. by 0·025 mm. with the spacing between the turns 1 to 2 mm. The electrical rating is approximately 12 amperes at 21 volts. For the higher temperature the outside diameter is 200 mm., the winding is rhodium strip, 6·3 mm. by

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[1] The Figures in this section are from a National Physical Laboratory pamphlet of the Department of Scientific and Industrial Research entitled *The Technique of Calibrating Platinum Thermocouples for use in Liquid Steel*, 1942, and our thanks are expressed to the Controller of H.M. Stationery Office for permission to use the figures and for information obtained from the pamphlet.

0·075 mm. with spacing of 1 to 2 mm. between turns and the winding on the central 150 mm. of the tube. Here the approximate electrical rating is 16 amperes, 17 volts.

In either case the electrical supply must be from a storage battery of at least 30 volts and with a maximum discharge rate not below 20 amperes ; a rheostat giving very smooth current control is an essential.

Determination of the Palladium Point. Palladium wire 0·5 mm. in diameter is used and should be the purest possible. To make the junction the two thermocouple wires are held horizontally and parallel about 3 mm. apart. The palladium wire is laid across the couple as shown in Fig. 9 (XXI[3]) so that the end A projects about 1 or 1½ mm. across the right wire and is at the same distance from its end. An oxy-coal gas jet is adjusted so as to be just hot enough to meet the palladium and is applied at the tip of the wire so as to melt it and fuse it to the wire of the couple. The end B is then cut and treated in the same manner. The wires of the couple are mounted in single-bore insulators of sintered alumina and are supported side by side and centrally in the vertical tube of the furnace in such a way that they do not touch the walls of the furnace tube ; about 25 mm. of the wires are left bare near the junction. Suitable tubes are 150 mm. long, 0·7 mm. diameter, and 0·5 mm. thickness. More than one couple can be calibrated at the same time. A control couple is inserted in the lower end of the tube (from below) ; here the wires may pass through a twin-bore insulator and the junction lies on the top of a refractory disk (of any suitable material) which just fits the tube. This control couple is fixed so that the disk lies about 15 mm. lower than the centre of the furnace tube and the bottom of the furnace is plugged with asbestos wool. The furnace is raised to 20° below the melting-point and the test-couples are lowered into position. The temperature is then kept steady and the test-couples are moved about in order to find the region in the tube where the most uniform temperature conditions prevail and are finally fixed at the centre of this region while the disk of the control couple is moved up so as

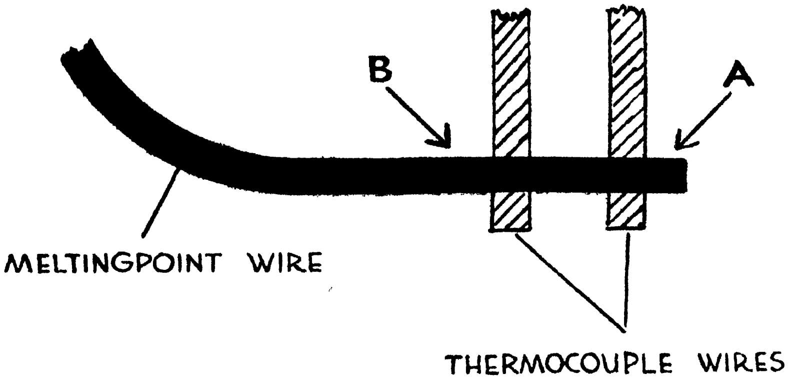

FIG. 9 (XXI[3])
Two thermocouple wires held horizontal and parallel and palladium wire lying across them

to be only a few millimetres away; in order to do this, accurate measurements of the lengths of the couples are made beforehand.

The current supply is now adjusted so that the temperature rises at the rate of $\frac{1}{2}$° to 1° per minute and readings of all the couples are taken in rotation and at equal intervals of time so that a complete cycle takes 1 minute. Thus with two test-couples and the control a reading will be taken every 20 seconds. As soon as the determination is completed, the thermocouples should be removed from the furnace and it should then not be necessary to shorten them by more than 5 mm. The kind of results obtained is shown in Fig. 10 (XXI[3]) in which the E.M.F. scale refers to the test-couples only, that of the control curve having been displaced so as to bring this curve near the others; this has also been done in Fig. 11 (XXI[3]).

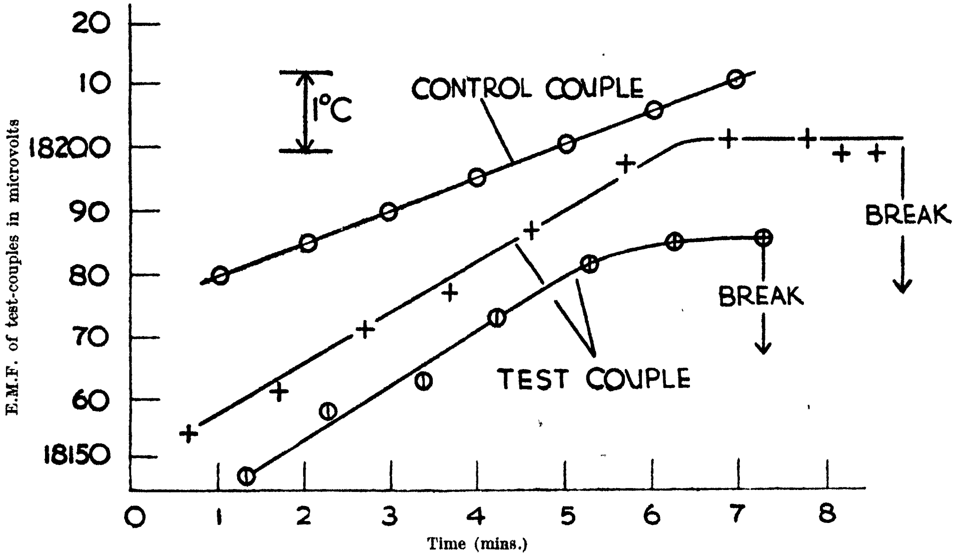

FIG. 10 (XXI[3])

The standard E.M.F. at the melting-point is 18,192 microvolts. The melting-point in the test is given by the horizontal part of the curve. In some cases the curve does not become horizontal and then the test is considered satisfactory if the slope of the curve decreases to one-third of the original slope, and in this case the melting-point is taken to be the higher end of the decreased rate—this is generally at the point where the junction breaks. Sometimes the palladium melts but does not break at once, in this case curves may be obtained in which the M.P. is given by the horizontal part of the curve and this is followed by a rise of temperature. When the wire melts, the E.M.F. does not fall immediately to zero but there is usually a residual E.M.F. which causes a galvanometer deflection of several centimetres; if the insulators touch one another or the walls of the tube this may impair the M.P. determination. If the observed E.M.F. does not differ from the standard value 18,192 microvolts by more than ± 30 microvolts, the deviation observed may be used as a correction over the range 1,500° C to 1,770° C, but if it is larger than this the platinum point should be determined.

Determination of the Platinum Point. Here the ends of the two wires of the test-couple are fused together in the oxy-coal gas flame. Proceeding in the same way as before the temperature of the furnace is raised to 20° below the M.P. of platinum. By moving the test-couple the hottest part of the furnace is discovered and the junction is located here. There are two reasons for this, first the junction will always be the hottest part of the test-couple, there will be a down gradient of temperature along the platinum wire from the junction so that the wire will not melt first at some point other than the junction, secondly the control couple will not be at the hottest part of the furnace and so its platinum wire will not melt before the test-junction does; but to ensure that this does not happen the disk bearing the control-junction is placed 20 mm. below the test-junctions. The curves obtained are normally similar to those shown in Fig. 10 (XXI^{3}) for palladium. The platinum arm first melts at the junction since this is the hottest part of the furnace and then as the temperature rises the melting advances along the wire; if the two wires are about 2 mm. apart the junction generally does not break but is held together by the surface tension of the liquid metal. In this way the junction moves along the alloy wire and the couple continues to record the melting-point.

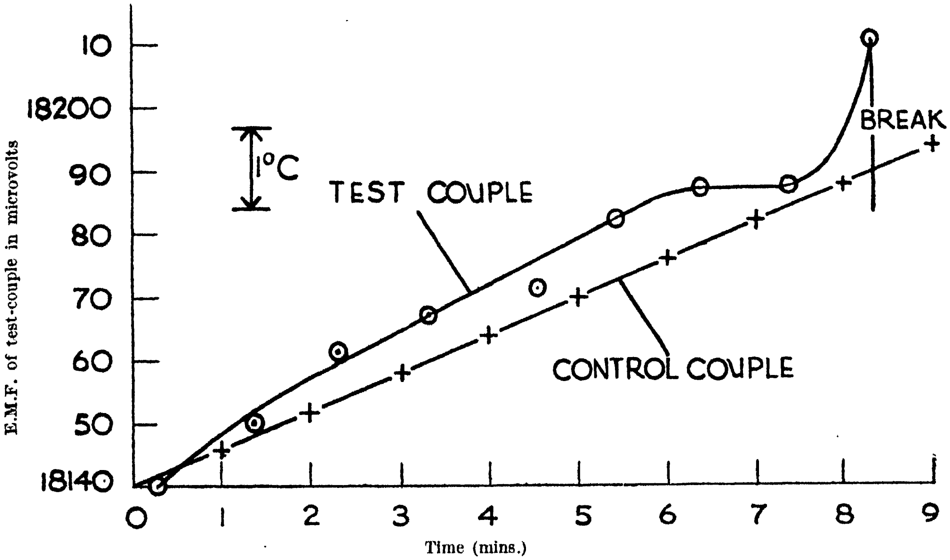

FIG. 11 (XXI^{3})

Sometimes a steady value is not given. A continuous rise indicates contamination of the thermocouple and 1 or 2 cm. of the ends of the wire should be removed and a new junction made. When the results are unsteady but do not show a continuous rise it is often possible to take a mean value which is satisfactory. The standard value is 21,114 microvolts.

Thermocouples for Technical Purposes. The E.M.F. generated by a thermocouple depends on the difference of temperature between the hot and the cold junction, so that if this E.M.F. is to be used to measure the temperature of one junction, that of the other (generally the cold one) must be both constant and known. In nearly all scientific work the cold junction is maintained by melting ice at a temperature of 0° C, or at room temperature by means of oil in a Dewar flask, or in an electrically heated enclosure thermostatically maintained at a constant temperature.

In industrial practice the cold junction would be at the head of the thermocouple, but since this is often subject to high and fluctuating temperatures it is desirable to move it to some position where more stable conditions exist. For industrial purposes the indicator or recorder itself is generally placed in such a position and the cold junction may be transferred to it by the use of compensating leads ; for use with platinum rhodium couples these may consist of wires of copper and an alloy of copper and nickel giving the same E.M.F. as that of the thermocouple itself. In the case of base metal thermocouples the connecting leads are frequently made of the same materials as the couples.

This arrangement has advantages since it is now possible to employ measuring instruments which are fitted with automatic compensators for changes in cold-junction temperatures. It has been found sometimes advantageous to bury the cold junction a few feet below the surface of the ground ; at a depth of 10 feet under a building the temperature remains remarkably constant throughout the year.

In industry the more general method of measuring the E.M.F. is that of the direct deflection of a galvanometer or millivoltmeter, the scale of which is calibrated to read temperatures directly. This instrument is usually of the double pivot moving-coil type, and is thus little affected by the stray magnetic fields or changes in level experienced in a workshop. It is advisable that the resistance of the galvanometer should be as high as possible, so that the resistance of the leads with temperature will have a negligible effect on the scale value of the galvanometer and hence on the accuracy of the readings obtained.

For the same reason it is important that the resistance of the galvanometer should alter as little as possible with changes of temperature. This is achieved by making the galvanometer coil of copper wire and placing in series with it a coil of manganin, which, although of high resistance, has a negligible temperature coefficient of resistance.

SECTION 2: DENSITY

The density of solids and liquids are considered in detail in Chapter XII, Vol. 1, Sections 2 and 3. The density of gases and vapours are dealt with in Chap. I, Vol. 2, Section 6. The use of some of these methods in micro-work will be reviews. An application of the displacement methods to a biological problem will also be considered. The density of water given in Vol. I, pp. 489–90, to the seventh decimal place can no longer be regarded as definite owing to the fact that when these determinations were made the possibility of the small amount of heavy water being present was unsuspected.

Micro-methods. The flotation method,[1] the balanced liquid method,[2] and the schlieren and various pyknometer methods [3] have also been adopted by others to micro-work. A review of these and related methods has been made by Alber [4] and also by Blank and Willard.[5] Alber [6] obtained specific gravities by three different methods: (1) standard 5-ml. pyknometer, weighed on an analytical balance with a sensitivity of 0·1 mg.; (2) decigram pipettes weighed on a semimicro-balance with a sensitivity of 0·01 mg.; (3) centigram and milligram pipettes, weighed on a micro-chemical balance with a sensitivity of 0·001 mg. A comparison of the S.G. micro-pipettes with the pyknometer can be seen from the following table:

Substance	Temperatures, ° C.	Specific gravities		
		Macro-pyknometer, 5 ml.	Decigram pipette, 0·1 ml.	Centigram or milligram pipettes
n-Pentane	20/4	0·6285	0·628	0·627
n-Heptane	20/4	0·6841	0·685	0·683
n-Butylamine	21/4	0·7400	0·740	0·739
Methyl alcohol	25/4	0·7864	0·785	0·785
Benzene	20/4	0·8790	0·878	0·877
Cyclohexanol	25/4	0·9562	0·954	0·954
Morpholine	20/4	0·9999	1·000	1·005
Aniline	20/4	1·0210	1·021	1·022
Glycerol	21/4	1·2440	1·240	1·245
1,2-Dibromopropane	22/4	1·9300	1·933	1·925
Ethylene bromide	21/4	2·1360	2·133	2·130
Bromoform	20/4	2·8930	2·889	2·890

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[1] Bernal and Crowfoot, *Nature*, 1935, *135*, 305.

[2] *Z. anal. Chem.*, 1936, *107*, 108.

[3] Emich and Schmeider, *Microchemical Laboratory Manual*, J. Wiley & Sons, N.Y., 1932.

[4] *Ind. Eng. Chem. Anal.*, 1940, *12*, 764.

[5] *J. Chem. Educ.*, 1935, p. 1220.

[6] *Loc. cit.*

The most suitable density procedure, according to Alber,[1] for small crystal fragments is the flotation method of Retgers [2] which by including centrifugation has been improved by Hendricks and Jefferson [3] and by Bernal and Crowfoot.[4] The latter method has been tested out by Alber [5] applying carbon tetrachloride, benzene, nitrobenzene, bromoform, and methylene iodide in their pure forms or in mixtures. After centrifuging for 5 minutes, the specific gravities of the reference liquids in which the crystals remained suspended were determined. The amount of material necessary varied over a wide range, between 50 and 250 micrograms, and the accuracy of the determinations, depending on the accuracy with which the specific gravity of the reference liquid was determined. Since the volumes of the latter after the separation from the solid phase were between 10 and 100 cu. mm., centigram and milligram pipettes were applied. Benzoic acid, naphthalene, and resorcinol gave results which agreed favourably with the values reported by Hendricks and Jefferson.[6]

The Displacement Method. A method has been devised by Lowndes to determine the density (accurate to the fourth decimal place),of a living aquatic organism without removing it from its environment.[7]

For volume determination, the adhering water necessitated an indirect method of determination. The basis of the solution of the problem was obtained from analogy with a method of determining the volume of a large irregularly shaped mixing-tank by determining the part of an added weighed salt (or chloride ion) in an aliquot portion of the total volume.

A density bottle is filled with sea-water and weighed. The aquatic organism is then inserted and the vessel reweighed, thus obtaining a displacement value. To find the volume of the organism, first wash out the contents of the density bottle into an excess of silver nitrate and weigh the halide and then again fill the same density bottle with the organism and sea-water and pour the sea-water into excess of silver nitrate and again weigh the halide. Provided the volume of the density bottle is known the exact volume of the organism is accurately obtained from the two weights of halide. The density bottle in the first case is washed out with distilled water, but in the second case the organism must be retained for a few seconds on a suitable sieve or filter and the adhering sea-water rinsed off—not with distilled water, however, on account of the difference in osmotic pressure, but it must be rinsed with a solution free from halides but isotonic with sea-water. With marine organisms the obvious non-halide isotonic solution is sodium nitrate, to which a little calcium nitrate is added. The divalent calcium ion has a marked effect in slowing up the ionic interchange between the fluids within the organism and its environment.[1] A solution of glucose could be used and in certain cases it provides a useful check but solutions of glucose do not keep well and in other cases it presents difficulties in the precipitation of the silver halides. At Plymouth the nitrate solution is made up in bulk and its preparation is as follows. 1,800 grams of sodium nitrate are dissolved in 8 litres of distilled water. 100 ml. of nitric acid are diluted and neutralized with precipitated calcium carbonate. The carbon dioxide is boiled off and the solution filtered into the nitrate solution. The *p*H of this solution is now about 6 and it must be brought down to that of sea-water by adding a few drops of a solution of sodium carbonate. The indicator used is cresol red and the adjustment is easily made for on adding the carbonate to the nitrate a precipitate is formed which at first readily dissolves on shaking, and it is simple with a little experience to judge the end-point. The solution is then made up to 10 litres and it will be found that 350 ml. of this solution made up to a litre will give a solution which is practically isotonic with the Plymouth sea-water. The osmotic pressure of both sea-water and the nitrate solution require checking.

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[1] *Ind. Eng. Chem. Anal.*, 1940, *12*, 764.

[2] *Neues. Jahrbuch Mineralogie*, 1889, *2*, 185.

[3] *J. Optical Soc. Amer.*, 1933, *23*, 299.

[4] *Nature*, 1934, *134*, 809; 1935, *135*, 305.

[5] *Loc. cit.*

[6] *J. Optical Soc. Amer.*, 1933, *23*, 299.

[7] Lowndes has made a special study of displacement methods of weighing living aquatic organisms, &c., and the following references by him should be consulted:

'The Density of Some Living Aquatic Organisms', *Proc. Linn. Soc. Lond.*, 1938, *150*, 62; 'The Displacement Method of Weighing Living Aquatic Organisms', *J. Mar. Biol. Assoc.*, 1942, *25*, 555–74; 'The Percentage of Water in Jelly-fish', *Nature*, 1942, *150*, 579; 'Density of Crabs and Lobsters', *Nature*, 1943, *151*, 336; 'Some Applications of the Displacement Method of Weighing Living Aquatic Organisms', *Proc. Zool. Soc. A.*, 1943, *113*, 28.

Example. The determination of the density of a common sponge with siliceous spicules and the density of its protoplasm.

The Sponge *Ficulina ficus.* This is a homogeneous sponge which can be cut cleanly under water and has much the appearance of cheese. The sponge is cut into thin elongated blocks which are packed into an ordinary wide-mouthed density bottle. Under these circumstances the sponge occupies a large proportion of the volume of the bottle and a titration can be substituted for a gravimetric estimation.

The weighed sponge is boiled with concentrated nitric acid and the spicules washed and filtered on to a weighed Gooch-asbestos filter, ignited and weighed. Assuming that the sponge consists of protoplasm and spicules only, the density of the former is obtained from the density of the whole sponge together with the weight and density of the spicules.

It is not justified generally in assuming that a sponge consists of protoplasm and spicules only, but the density of the other living tissues is so close to that of the protoplasm that the assumption is allowable so far as density is concerned. This does not apply to all sponges. The figures are as follows:

Temperature	14·4°
Density of sea-water	1·02657
Volume of density bottle	43·8523 ml.
Sea-water	44·9536 grams
Sea-water and sponge	46·0776 grams.
Titrations with N/10 silver nitrate	23·20 ml. and 13·86 ml.
Volume of sponge	17·6543 ml.
Water displaced by sponge	18·1234 grams
Water remaining in bottle	26·8302 grams
Weight of sponge	19·2474 grams
Density of sponge	19·2474/17·6543 = 1·09023

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[1] Pantin, 'The Adaptation of *Gunda Ulvae* to Salinity: iii. The Electrolytic Exchange', *Jour. Exp. Biol.*, 1931, *8*, 94.

Density of Protoplasm (D):

$D = (W - M)/(V - M/2{\cdot}65)$. Where W = weight of sponge, V = volume of sponge, M = weight of spicules, and 2·65 = density of Silica.

Density of protoplasm	1·0566
Weight of spicules	0·9865 grams.

Since protoplasm, taking the term in its broadest meaning, comprises about 80 per cent water, its density will vary considerably with the temperature. Using gravimetric methods throughout, its density at 15·0° is 1·0565.

SECTION 3: PRESSURE

Units of Pressure (*see* Vol. I, p. 559). In [C.G.S.]-system the unit of pressure is 1 dyne per sq. centimetre = 1 (chemical) bar = 1 microbar. In barometric work a practical unit has been introduced. That is the 'bar' (b.); it is 1,000,000 times the (chemical) bar above or 10^6 dynes/cm.^{2} (one megadyne per sq. centimetre). From this has been defined

1 millibar (= 1 mb.) = 1,000 (chemical) bar [C.G.S.] = 1,000 dynes per sq. centimetre
,, = 0·001 bar (practical unit)

One thousand millibars are equivalent to the pressure of a column of mercury 750·1 mm. high at 0° C. in latitude 45°.

The millibar as a measure of atmospheric pressure has been in general use in the Meteorological Office, London, since May 1, 1914, and modern barometers are already divided in millibars (¾ mm., exactly 0·75006 mm.) instead of millimetres or inches.

Expressing the pressure p by the length of a vertical column of liquid balancing it, we have:

$$p = s(1 - \alpha_1 t)b.g \text{ bar [C.G.S.]}$$

where s = spec. weight of the liquid at 0°
α_1 = cubical coefficient of thermal expansion of mercury
t = temperature in degrees
b = length of the column in centimetres
g = acceleration due to gravity in cm./sec.^{2}

For mercury $s = 13{\cdot}5955$, $\alpha_1 = 181{\cdot}6.10^{-6}$. According to convention g is referred to as the acceleration due to gravity in latitude 45° and at sea-level (= $g45$); $g45 = 980{\cdot}617$ cm./sec.^{2} and is called 'normal gravity'.

We obtain the so-called 'pressure reduced to 0° and normal gravity' (= b_0) as follows:

$$p = s.g45.b(1 - \alpha_1 t)\frac{g}{g45} = s.g45.b_0 = 13{\cdot}33202.b_0 \text{ mb.}$$

where $b_0 = b(1 - \alpha_1 t)\dfrac{g}{g45}$

b_0 is therefore the length of the column (measured at the temperature t and with g) at 0° and with $g45$ computed from the equation

$$b_0(1 + \alpha_1 t).g45 = b.g.$$

where in the *free air*:

$$g = g45(1 - 0{\cdot}00259 \cos 2\varphi)\left(1 - \frac{2h}{\mathrm{R}}\right) \text{ in C.G.S. units}$$

$g45 = 980{\cdot}617$ cm./sec.^{2}
h = height in metres
φ = latitude
R = radius of the earth = 6,370,000 metres

For accurate reading the expansion of the scale must be taken into consideration (*see* section 'Barometer Corrections for Temperature')

$$b_0 \frac{1 + \alpha_1 t}{1 + \alpha t} = b\,; \quad b_0 = \left(1 - \frac{\alpha_1 - \alpha}{1 + \alpha_1 t} t\right) . b . \frac{g}{g45}$$

Taking α (linear coefficient of expansion) for brass (0·0000184) or gold (0·0000138) according to the scale on brass or gold.

In the International Tables the following formula of g is used for correcting the station level pressure of places on mountains to standard gravity.

$$g = 980{\cdot}617(1 - 0{\cdot}00259 \cos 2\varphi)\left(1 - \frac{5h}{4\mathrm{R}}\right)$$

The Kew Barometer (*see* Vol. I, p. 563). A now widely used and very convenient model of barometer is that known as the Kew instrument. It does not need zero adjustment. The scale is graduated in such a way that the changes of the level in the cistern are automatically allowed for. Since it is not necessary to see the mercury in the cistern of such barometers the cistern itself consists of a solid, non-transparent cup. A further advantage of this barometer is that it can be transported in horizontal position. It indicates the correct pressure, however, only when the amount of mercury remains constant, besides it needs very careful manufacturing and comparison with a normal barometer.

Hypsometer. Hypsometers are thermometers which are used for determining the pressure. They measure the boiling-point (of distilled water) which temperature is a function of the pressure (altitude).

The hypsometer consists of a boiling-vessel with a vapour mantle and a special thermometer. Above the bulb the thermometer has a chamber so that the stem covers only the range from say 95 to 105° C. The graduation is in 1/100° C. so that 1/1000° C. can be estimated, corresponding to about 25–30 cm. altitude variation. For convenience such hypsometric thermometers are supplied with direct pressure scales in millimetres or millibars.

Hypsometers are excellent instruments for checking mercury barometers, e.g. after transport for journeys, &c., but they have to be of high quality. They were used by O. Hecker for determining the gravity at sea. Electrically heated hypsometers equipped with mercury thermometers or resistance thermometers are in use for direct reading or recording purposes. Compared with aneroid barometers or barographs they have the advantage of being free of elastic errors and temperature influence, but they are only used for special purposes (e.g. in aircraft).

The Barograph (*see* Vol. I, p. 565). Fig. 12 (XXI^3) shows a modern form of barograph.

The fundamental feature of this instrument is the closed 'vacuum box' of nickel-silver or other alloy, the top and bottom of which are two thin corrugated disks and which is nearly completely evacuated of air. Due to the external pressure this box is deformed until the elastic force in the walls of the box or (in the still popular and older system) those of the springs contained in the box or connected with the top of the box outside are balanced.

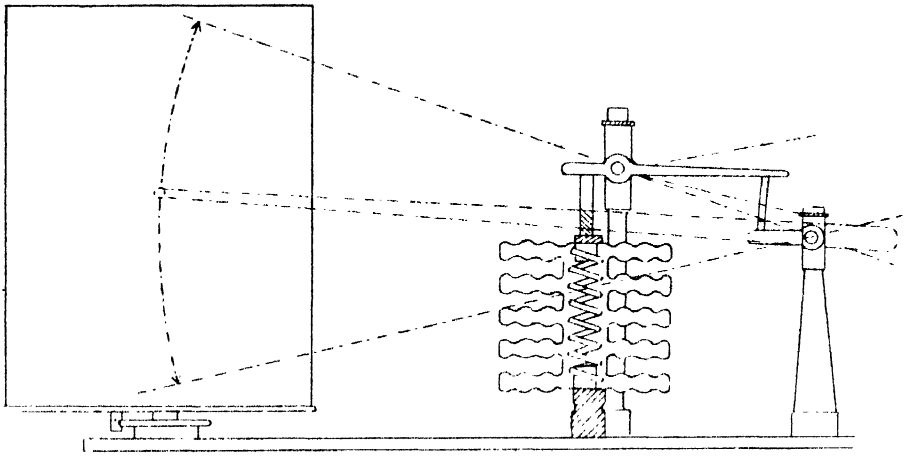

FIG. 12 (XXI^3)
A barograph

Every pressure variation produces a new equilibrium position. The small movements of the top of the box (or set of boxes) or the spring thus produced are mechanically or optically magnified and may be read either on a scale or recorded on a chart fitted to a drum (*see* barograph). The calibration of the aneroid barometer is carried out by a standard thermometer. The readings are independent of gravity.

SECTION 4: HARDNESS

The 'hardness' of a substance bears a relationship to the moduli of elasticity of that substance. There is some difficulty in formulating this relationship in an exact form. Carduollo[1] writing on this topic states:

> The logical solution of the difficulty seems to be to take the principal dimensional properties involved in the idea of hardness, to write an equation of rational form connecting these properties with a numerical value for hardness, to determine experimentally whether this equation is consistent, and the value of its constants, and to accept this equation as the definition of hardness. It is obvious that the principal dimensional properties affecting the hardness of a homogeneous material are its elastic limit and modulus of elasticity. The simplest form of equation that we can write connecting hardness with these properties is
>
> $$H = CE^{m}L^{n}$$
>
> where H = numerical value of hardness
> C = constant
> E = modulus of elasticity
> L = compression elastic limit
> m and n = small positive real indices

There are, however, certain materials, such as glass, which do not conform to the above equation. This may be explained by the peculiar atomic structure of glass, which does not exhibit a regular geometric pattern, but has individual molecules of the various constituents scattered haphazardly throughout. Nevertheless, as Carduollo says, 'we may be warranted in holding to the equation given, in the case of all materials of crystalline structure which are capable of plastic deformation, and in ignoring those extremely brittle materials of amorphous structure on the ground that we have available no real information with regard to their elastic limits'.

Perhaps the best definition of hardness, as such, arises from a consideration of its physical manifestations, that is to say, as that property of substances which is determined by their resistance to abrasion and indentation by other substances, or by their ability to abrade and indent those other substances.

Scale of Hardness

The first systematic classification of substances on a graded hardness scale was carried out by the mineralogist Mohs in 1822. Mohs' *Hardness Scale* is occasionally used for purposes of approximate classification in particular by mineralogists. Constructed from a series of experiments which involved a 'scratch method' of measurement, it lists ten minerals in order of hardness, beginning with the softest and ending with the hardest.

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[1] *Mechanical Engineering*, October 1924, quoted from 'Hardness', Landau Nitralloy Corp., New York, 1943. The two figures are also from this pamphlet by permission.

MOHS' HARDNESS SCALE

1. Talc
2. Gypsum
3. Calc spar
4. Fluorspar
5. Apatite
6. Feldspar
7. Quartz
8. Topaz
9. Ruby, sapphire
10. Diamond

The invention of the sclerometer by Seebeck in 1833 was the first step to putting hardness measurement on a scientific basis. This instrument carried a loaded point which moved across the surface of the specimen, thus producing a scratch. It could be used to determine hardness either by measuring the minimum weight on the point (moving under a fixed tangential force) necessary to produce a scratch visible under certain fixed conditions of illumination, or by measuring the dimensions of the scratch produced by a given load on the point.

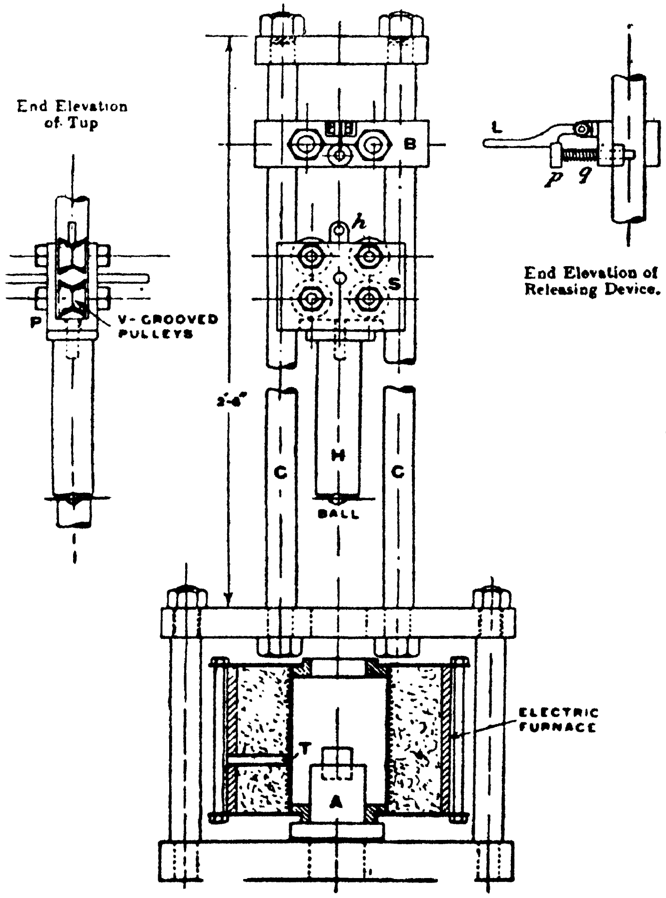

FIG. 13 (XXI[9])
Brinell impact machine or dynamic hardness tester

In succeeding years, various developments of the sclerometer principle were introduced by different workers, as well as hardness testers which measured by compression, penetration, dynamic impact and other means, but the invention of the Brinell hardness meter quickly rendered all these instruments obsolete.

Brinell Apparatus

This is an apparatus (Fig. 13 (XXI[3])) for making an indentation with a hard steel ball, and means for measuring the diameter of the indentation. The so-called Brinell hardness number is obtained by dividing the load in kilograms on the ball by the area in square millimetres of the impression. Modifications since introduced employ a cone or pyramid as indentor, while carborundum or even diamond may be used instead of steel for the material of the indentor. One model of the machine consists of a

heavy cast iron frame, an adjustable anvil, and a hydraulic press. The specimen is placed on the anvil, and is brought into contact with a ball of 10 mm. diameter attached to a plunger, which in turn is connected to the ram of the hydraulic press. A hand-pump is used to force oil into the hydraulic press. The resulting compressive force set up between the ball and the specimen may be read off approximately on a pressure gauge.[1]

If it be assumed that the surface of the ball remains spherical under the conditions of the test, the Brinell number (H) is given by the formula

$$H = \frac{2P}{\pi d^2}\left(1 + \sqrt{1 - \left(\frac{d}{D}\right)^2}\right)$$

where P = load in kilograms
D = ball diameter in millimetres
d = indentation diameter in millimetres

In giving the Brinell number, both P and D must be specified as well as the material of the indentor.

The causes of discrepancies in the determination of the Brinell number have been classified under the following headings :

I. Apparatus and Procedure
- (*a*) Rate of applying load
- (*b*) Time under nominal load
- (*c*) Error in load
- (*d*) Error in measuring diameter of indentation

II. Specimen
- (*a*) Non-uniform properties
- (*b*) Curvature of surface
- (*c*) Thickness
- (*d*) Spacing of indentations
- (*e*) Angle between load line and normal to specimen

III. Indenting Ball
- (*a*) Error in diameter
- (*b*) Non-spherical shape
- (*c*) Deformation of ball under load-elastic deformation and permanent deformation[2]

The original paper of Petrenko, Ramberg, and Wilson should be consulted for detailed study of these varying factors. The procedure finally adopted by these authors was as follows:

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[1] *J. Res. Nat. Bur. Standards*, 1936, *17*, 59.

[2] *Ibid.*

(*a*) The loading mechanism should be operated to give a uniform rate of loading not exceeding 500 kg./sec.

(*b*) The maximum load should be applied for 30 seconds.

(*c*) The error in the load applied by the machine should not exceed $\frac{1}{3}$ per cent. This should be checked by periodic calibration with a proving ring or other suitable device.

(*d*) The calibration of the apparatus used for measuring the diameter of the indentation should be checked frequently. The maximum error in the reading at any point on the scale should not exceed 0·01 mm. The indentation diameter should be read in two or more mutually perpendicular directions.

The standard ball and loads[1] used for Brinell Hardness Testing shall be as follows:

Diam. of ball mm.	Load			
	$\frac{P}{D^2} = 1$ kg.	$\frac{P}{D^2} = 5$ kg.	$\frac{P}{D^2} = 10$ kg.	$\frac{P}{D^2} = 30$ kg.
1 . . .	1	5	10	30
2 . . .	4	20	40	120
5 . . .	25	125	250	750
10 . . .	100	500	1000	3000

Notes.—(i) In the case of materials of coarsely duplex micro-structure such as cast iron, care should be taken to make a sufficiently large impression and wherever possible a number of impressions should be made and an average taken.

(ii) The same Brinell hardness number is given by tests on the same uniform material with balls of different diameters when the same value of the ratio $\frac{P}{D^2}$ is used.

Rockwell Hardness Tester

This apparatus utilizes the same principle as the Brinell apparatus. It makes two successive indentations on a specimen, the load being increased in the second case, and the difference in depth is the basis for calculation of the Rockwell hardness number. Two penetrators are commonly used with this instrument—the 'Brale' penetrator, a sphero-conical diamond, for all hard substances, and for softer materials a steel ball of diameter $\frac{1}{16}$ in. is employed. Two scales on the dial which gives the Rockwell hardness number directly, differentiate between the two penetrators.

The United States Bureau of Standards has worked out a set of formulae which give the relation between Brinell and Rockwell hardness. These formulae, however, may give errors of ± 10 per cent. They are as follows:

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[1] ***British Standard Method and Tables for Brinell Hardness Testing,*** **British Standards Institution, No. 240, 1937.**

Let B = Brinell hardness numbers
R_b = Rockwell value with steel penetrator
R_c = Rockwell value with diamond penetrator

Then for R_b (ranging from 40 to 100)

$$B = \frac{7{,}300}{130 - R_b} \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(A)}$$

For values R_c (from 10 to 40)

$$B = \frac{1{,}520{,}000 - 4{,}500R_c}{(100 - R_c)^2} \quad . \quad . \quad . \quad . \quad . \qquad \text{(B)}$$

For values of R_c (from 40 to 70)

$$B = \frac{25{,}000 - 10(57 - R_c)^2}{100 - R_c} \quad . \quad . \quad . \quad . \qquad \text{(C)}$$

The two instruments dealt with above measure static hardness. Machines have also been devised to measure dynamic hardness by the rebound of an impactor or tup from the surface of the specimen. These machines are called Sclerographs or Scleroscopes, and have been widely adapted on the

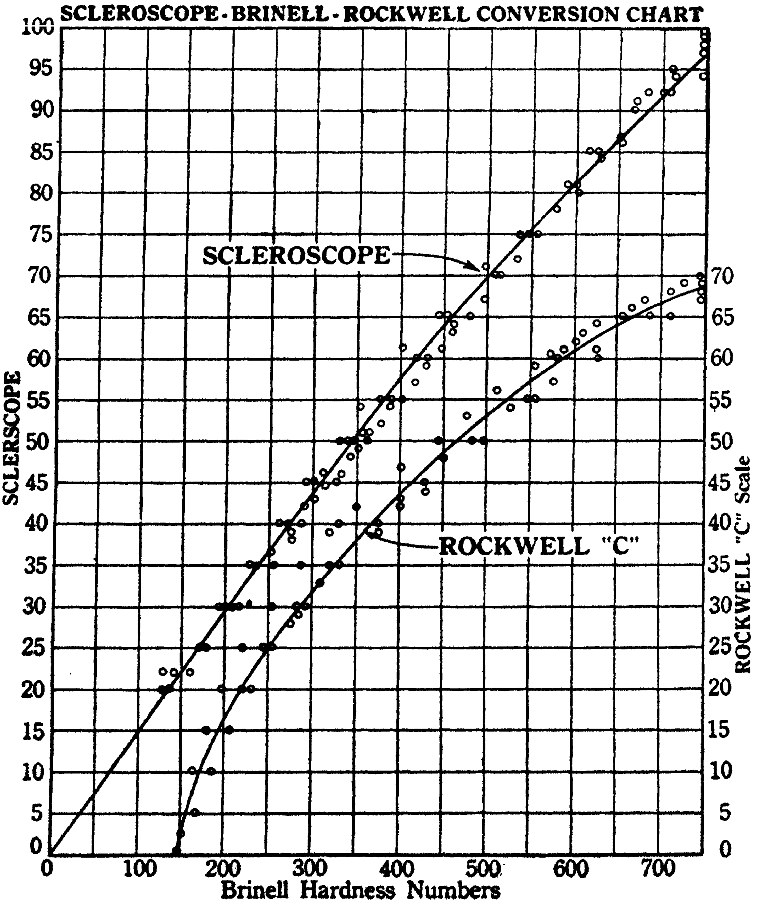

FIG. 14 (XXI[3])

Relation between Brinell hardness numbers, Rockwell 'C' scale, and Shore scleroscope

Continent. One particular model employs as impactor a small steel hammer, with a diamond at the lower end. This hammer travels vertically in a glass tube carrying a scale by which the height of rebound of the hammer can be ascertained.

Fig. 14 (XXI^3) shows the relation between Brinell hardness numbers, Rockwell ' C ' scale, and Shore scleroscope furnished by the Shore Instrument Company. The curve was plotted from eight different conversion charts including those of the American Society of Metals, International Nickel Company, The Heppenstall Company, Firth Sterling Company, Lindberg Engineering Company, Rockwell, and *Iron Age*.[1]

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[1] 'Hardness'. Nitralloy Corporation, N.Y., 1943, p. 73.

SECTION 5: CALORIFIC VALUES FROM ANALYSIS

The calorific value of a coal having a dry ash-free volatile content of over 20 per cent can be calculated to a good degree of accuracy by means of the formula developed by D. J. Ryan[1] from a study of the proximate analyses of several hundreds of coals.

$$\text{Calorific value} = (16{,}990 - 52{\cdot}8V^1)\left\{\frac{100 - (1{\cdot}1A + M)}{100}\right\}$$

where V^1 = dry ash-free volatile
A = per cent ash
M = per cent moisture

The above formula gives the calorific value of a coal in B.Th.U.s per lb.

Example. A coal tested according to the British Standard Specification gave the following results:

Moisture	2·2 per cent
Volatile less moisture	33·6 ,, ,,
'Fixed carbon'	58·3 ,, ,,
Ash	5·9 ,, ,,
Calorific value	13,790 B.Th.U.

Application of formula :

$V^1 = 36{\cdot}6$ (calculated dry ash-free volatile)

$$(16{,}990 - 52{\cdot}8V^1) = 15{,}063$$

$$\left\{\frac{100 - (1{\cdot}1A + M)}{100}\right\} = 0{\cdot}9131$$

$\therefore$ *Formula calorific value* $= (15{,}063 \times 0{\cdot}9131)$
$= 13{,}750$ B.Th.U.s per lb.

It will be noted that the term 'fixed carbon' is not included in the new formula.

The ash multiplied by 1·1 is taken to represent the 'real' mineral matter present in the coal before incineration.

The factor $\left\{\frac{100 - (1{\cdot}1A + M)}{100}\right\}$ in the new formula represents the fraction of 'pure coal' substance present in any coal.

The term V^1, the dry ash-free volatile figure, is employed in the formula because it is possible to compare the equality (or otherwise) of the 'pure coal' substance present in a coal on this basis. For example, if we have two coals, A and B, with the following proximate analyses

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[1] Private communication.

	Moisture	Vol.	Ash	'Fixed carbon'
A . . .	5·0	31·0	6·0	58·0
B . . .	13·0	25·1	15·0	46·9

It is not easy to visualize that both contain the same type of 'pure coal' substance; yet, if we calculate the V^1 for both coals we will find it 34·8 per cent for each coal.

In the new formula it is assumed that all coals having identical V^1 contents and having the same fraction of 'pure coal' present, will have equal calorific values. The formula also assumes that a hypothetical dry ash-free volatile-free coal has a calorific value of 16,990 B.Th.U.s per lb. This figure is numerically equal to the calculated heating value of a (hypothetical) coal composed entirely of carbon and hydrogen in the ratio of 15·6 : 1. This is the average ratio in which these elements occur in bituminous coals. In calculating the figure 16,990, it was assumed that 1 gram of carbon in the form of β-graphite will evolve 7,900 calories when burnt to carbon dioxide, and that 1 gram of hydrogen when burnt to water vapour will evolve 34,500 calories. The calculated calorific value of this hypothetical coal is 9,440 calories per gram or 16,990 B.Th.U.s per lb.

The formula also assumes that the calorific value of a dry ash-free coal decreases by 52·8 B.Th.U.s for each increase of 1 in the value of V^1. This figure of 52·8 was arrived at in the following manner: The dry ash-free calorific values of 400 coals were calculated from known analyses; these values were subtracted from 16,990, and the differences were divided by the respective V^1 content of each coal. The average value of the 400 quotients thus obtained was 52·8.

Summary. The following is a summary of the errors obtained by the formula when applied to the analysis of 378 coals:

Table No.	No. of coals	No. of cases formula error is:					
		1 per cent	1–2 per cent	2–3 per cent	3–4 per cent	4–5 per cent	5–7 per cent
1	50	36	10	3	1	—	—
2	59	36	19	4	—	—	—
3	44	9	11	13	9	1	1
4	14	2	3	5	4	—	—
5	13	7	5	1	—	—	—
6 and 7 . . .	41	23	11	6	1	—	—
8	18	7	6	5	—	—	—
9	37	18	11	6	2	—	—
10	102	63	31	4	2	2	—
Total	378	201	107	47	19	3	1
Per cent . . .	100	53	28·4	12·5	5	0·8	0·3
Cumulative . .	Per cent	53	81·4	93·9	98·9	99·7	100·0

It will be seen that the formula gives results which vary from the bomb value by :

less than 1 per cent	*in 53*	*cases*	*out of 100*
,, ,, *2 per cent*	,, *81*	,,	,, *100*
,, ,, *3 per cent*	,, *94*	,,	,, *100*
,, ,, *4 per cent*	,, *99*	,,	,, *100*

The formula does not give reliable results when applied to coals having a dry ash-free volatile content of less than 20 per cent. For *these coals* Ryan has developed the following formula :

Calorific Value = (84F.C. + 100V) calories per gram
where F.C. = per cent fixed carbon
and V = volatile less moisture content

This formula gives good success in predicting the calorific values of 'low-volatile' coals.

American Coals. From a study of the published analyses of 66 representative American bituminous and semi-bituminous coals, Ryan has developed the following formula :

Calorific Value (100V + aC) B.Th.U.s per lb.
Where V = volatile per cent
C = fixed carbon
and the constant $a = 181$ for bituminous coals
and $a = 170$ for semi-bituminous coals

This simple formula for American coals gives good results.

Note regarding Accuracy of Bomb Calorific Values. As regards the accuracy of the bomb calorimeter for determining the calorific values of coals it is of interest to quote the following paragraph from the British Fuel Research publication No. 29 entitled 'An Investigation of the Accuracy of Routine Analytical Determinations on Coal and Coke' (p. 15) :

> The figures for calorific value of coal considered on an air-dried basis show that in the majority of cases duplicate determinations should not differ by more than 90 B.Th.U.s. When comparing coals of this type on the basis of calorific values, however, little if any significance attaches to differences which are less than 60 B.Th.U.s if the determinations have been performed in duplicate or less than 100 B.Th.U.s if the figures only represent single observations.

In 1936 the Fuel Research Board sent a sample of a single coal to twelve laboratories. The extreme difference between the laboratories as regards the calorific values returned was 130 B.Th.U.s.[1]

(*N.B.* The empirical formulae for British coals can only be expected to give good agreement with the bomb value when the coal is analysed according to British Standard Specification methods. Similarly the formula for American coals is only applicable to analyses made according to A.S.T.M. methods.)

A Résumé of Various Formulae. There are several formulae for calculating the calorific value from either the ultimate or proximate analysis.

(1) *Calculation from the Ultimate Analysis*

In the following formulae the significance of the symbols used is as follows: C = per cent carbon; H = per cent hydrogen; O = per cent oxygen; N = per cent nitrogen; S = per cent sulphur.

---

[1] *Fuel Research Paper*, No. 44.

Dulong's formula:

$$\text{Calorific value} = 80{\cdot}80\text{C} + 344{\cdot}6\left(\text{H} - \frac{1}{8}\text{O}\right) + 22{\cdot}5\text{S}$$

Dulong's formula as modified by Berthelot:

$$\text{Calorific value} = 81{\cdot}37\text{C} + 345\left[\text{H} - \frac{(\text{O} + \text{N}) - 1}{8}\right] + 22{\cdot}2\text{S}$$

Mahler formula:

$$\text{Calorific value} = 81{\cdot}40\text{C} + 345\text{H} - 30(\text{O} + \text{N})$$

Steuer's formula: [1]

$$\text{Calorific value} = 81\left(\text{C} - \frac{3}{8}\text{O}\right) + 57 \times \frac{3}{8}\text{O} + 345\left(\text{H} - \frac{\text{O}}{16}\right) + 25\text{S}$$

Grummell and Davies' formula: [2]

$$\text{Calorific value} = (3{\cdot}635\text{H} + 235{\cdot}9)\left\{\text{C} + \text{H} - \frac{(\text{O} - \text{S})}{8}\right\}$$

(2) *Calculation from the Proximate Analysis*

In the following formulae the significance of the symbols used is as follows: C = per cent 'fixed carbon'; V = per cent volatiles less moisture; V′ = per cent volatiles in dry ash-free coal; M = per cent moisture; A = per cent ash.

Goutal formula: [3]

$$\text{Calorific value} = 82\text{C} + a\text{V}$$

where a is a variable factor depending on the volatile yield calculated to the dry ash-free coal (V′). The values of a corresponding to the values of V′ are given in the following table:

FACTORS FOR GOUTAL'S FORMULA

V′	a	V′	a	V′	a
1–4 . . .	100	17 . . .	113	30 . . .	98
5 . . .	145	18 . . .	112	31 . . .	97
6 . . .	142	19 . . .	100	32 . . .	97
7 . . .	139	20 . . .	109	33 . . .	96
8 . . .	136	21 . . .	108	34 . . .	95
9 . . .	133	22 . . .	107	35 . . .	94
10 . . .	130	23 . . .	105	36 . . .	91
11 . . .	127	24 . . .	104	37 . . .	88
12 . . .	124	25 . . .	103	38 . . .	85
13 . . .	122	26 . . .	102	39 . . .	82
14 . . .	120	27 . . .	101	40 . . .	80
15 . . .	117	28 . . .	100		
16 . . .	115	29 . . .	99		

Extrapolation must be resorted to, when the value of V′ exceeds 40. For anthracite the value of a is taken as 100.

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[1] *Brennstoff-Chemie*, 1926, *7*, 344.

[2] *Fuel*, 1933, *12*, 199.

[3] *Compt. rend.*, 1902, *135*, 477.

Nakamura formula : [1]

$$\text{Calorific value} = a\left(V - \frac{A}{10}\right) + 78C$$

where a depends on V and on the caking quality of the coal. The values of a in the Nakamura formula are given in the following table :

V	20-25	25-35	35-37·5	37·5-40	40–42·5	42·5–45	45-47·5	47·5–50
1 . . .	—	—	60	60	64	64	68	68
2 . . .	—	—	68	68	70	70	73	73
3 . . .	—	—	75	76	78	79	80	81
4 . . .	—	84	84	84	85	86	87	88
5 . . .	125-116	116–110	98	96	96	95	95	96

The formula has not been applied to non-caking coals yielding less than 35 per cent volatiles (V′) calculated on the dry ash-free basis. According to Nakamura the formula is only applicable to coals which yield over 20 per cent volatiles.

Ryan formulae : [2]

$$\text{B.Th.U.s per lb.} = (16{,}990\text{–}52{\cdot}8V')\left[\frac{100 - (1{\cdot}1A + M)}{100}\right]$$

The formula is not applicable to coals yielding less than 20 per cent volatiles calculated on the dry ash-free basis. Like the White formula for American coals and the Nakamura formula for Japanese coals, the Ryan formula applies to British coals only.

For American coals Ryan proposes the following formula :

$$\text{B.Th.U.s per lb.} = 100V + aC$$

where a is a constant. For bituminous coals $a = 181$; and for semi-bituminous coals $a = 170$.

Application of Empirical Formulae. A good empirical formula should afford a means of calculating the calorific value with a degree of accuracy which approximates closely to the bomb results, and its use should to a good extent dispense with the routine determinations of calorific values. A good empirical formula also places in the hands of the chemist a useful method for checking his analytical results, for if there is a serious discrepancy between the determined and calculated calorific values, an error is likely to have occurred either in the determination of the calorific value, or in the analysis of the coal. Because of the fact that proximate analyses of coals are more often made than ultimate analyses, empirical formulae based on the former analyses should have a greater application in industrial laboratories.

Note on the Julius Peters Bomb (*see* Vol. I, p. 424). This combustion bomb in general construction resembles the Kroeker bomb. The body, cap and cover of the bomb are made from special stainless steel.

The cap carries the inlet valve, an outlet valve and an insulated firing plug. The cap also carries the supports for the crucible and ignition wire.

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[1] *Jour. Fuel Soc. of Japan*, 1929, *8*, 119.

[2] Private communication.

One of these supports carries a shield which protects the charge in the crucible from risk of disturbance by the incoming stream of oxygen during the filling of the bomb. The cap rests on a shoulder situated internally in the body at a short distance from the top of the bomb. The bomb is sealed by means of a rubber washer and a steel washer, which together with the cap are held in position by the cover B which is screwed externally by hand for a short distance over the bomb. The steel washer is thus pressed home against the rubber washer.

The inlet valve is of the non-return type. The cap is free to move axially outwards under the pressure of the gas ; the rubber washer is further compressed and expands laterally against the wall of the bomb, making a perfect seal. The cover of the bomb cannot be unscrewed until the pressure is released.

SECTION 6: THERMAL PROPORTION

Heat of Vaporization (*see* Vol. I. pp. 447–8). Empirical formulae for computing latent heats of vaporization have been recorded by Meissner.[1] In addition to Trouton's rule they included the formulae of Nernst [2] and Bingham.[3] Hildebrand [4] proposed a relationship which is not limited to heats of vaporization at one atmosphere. He claimed that the molal entropy change of a liquid being vaporized is a unique function of the molal vapour concentration. Lewis and Weber [5] and McAdams and Morrell [6] published charts based upon the Hildebrand relation, showing molal entropy changes plotted as ordinates against (1000 P/T), a factor which is proportional to the vapour concentration when the perfect gas laws apply. Inspection of these charts shows that, while chemically similar substances group close together to form a single line, the spread between lines of dissimilar substances is considerable. Hence data on chemically similar substances must be available before these methods may be applied to any given liquid. Moreover, it has been found that the Hildebrand correlation breaks down at high temperatures and pressures. For wide ranges of temperature Watson's [7] correlation gives more accurate records of heats of vaporization.

Determination of the Latent Heat of Vaporization of a Liquid. If the liquid boils at a temperature much above the room temperature it is usual to condense the vapour in the calorimeter and from the rise of temperature produced to calculate the latent heat of condensation. On the other hand, when the boiling-point is not far removed from room temperature a known amount of the liquid can be vaporized in a calorimeter and the cooling produced be used to calculate the latent heat of vaporization.

The heat of vaporization can be obtained accurately by an electrical method using the technique and apparatus of Mathews, Fig. 15 (XXI^3).[8] The vaporizer B containing the liquid under examination consists of a small glass tube 26 mm. in diameter and 125 mm. long. At the top it was constricted to a small orifice 3 mm. in diameter. A reflecting surface, obtained by coating the outside of the vessel with silver, aided in preventing heat exchange to or from the vessel by radiation. Two heavy platinum wires sealed into the base of the vaporizer served as terminals of the heating-coil. These two heavy platinum wires dip into mercury cups, in order to complete the electrical circuit. The heating-coil (resistance 5 to 8 ohms) consists of a helix of fine platinum wire set in a vertical position. It is supported on a light mica frame, not shown in the diagram.

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[1] *Ind. Eng. Chem.*, 1941, *33*, 1440.

[2] *Theoretical Chemistry*, tr. of 6th German ed., London, Macmillan Co., 1914.

[3] *J. Amer. Chem. Soc.*, 1906, *28*, 723.

[4] *Ibid.*, 1915, *37*, 970.

[5] *Ind. Eng. Chem.*, 1922, *14*, 485.

[6] *Ibid.*, 1924, *16*, 375.

[7] *Ibid.*, 1931, *23*, 361.

[8] *J. Amer. Chem. Soc.*, 1926, *48*, 562.

Two small platinum wires sealed into the neck of the vaporizer (forming small hooks) afforded a means of attaching the vaporizer to a fine brass suspension wire, which leads to one arm of an analytical balance placed above the entire apparatus. The vessel at the bottom serves as a boiler for the generation of the vapour used to jacket the vaporizer. This is sealed into the chamber A in which the vaporizer is suspended. Some of the same liquid as that contained in the vaporizer is placed in the boiler and a current of from 6 to 8 amperes is passed through the resistance coil in the cistern H at the bottom of the boiler.

The cap C also is constricted at the top and has a 3 mm. hole for the passage of the suspension wire. The outer vessel D consists of a large cylindrical tube open at the bottom and constricted at the top, with an orifice 3 mm. in diameter. By means of a tubulure on the boiler, connexion is made with the condenser F. The outer vessel D rests in an annular ring of mercury contained in a channel cut in the cork K, and this vessel is also connected to the return condenser.

Electrical contact with the terminals of the heating-element in the vaporizer and the outside circuit is furnished through the two tubes I which are filled with mercury. Heavy amalgamated platinum wires, sealed into the lower ends of these tubes, extend into mercury cups providing contact with an outside electrical circuit which contains a potentiometer and a standard resistance. The upper ends of the tubes I are flanged out into cups 13 mm. in inside diameter, thus providing a fairly flat surface of mercury into which dip the platinum wires L from the vaporizer.

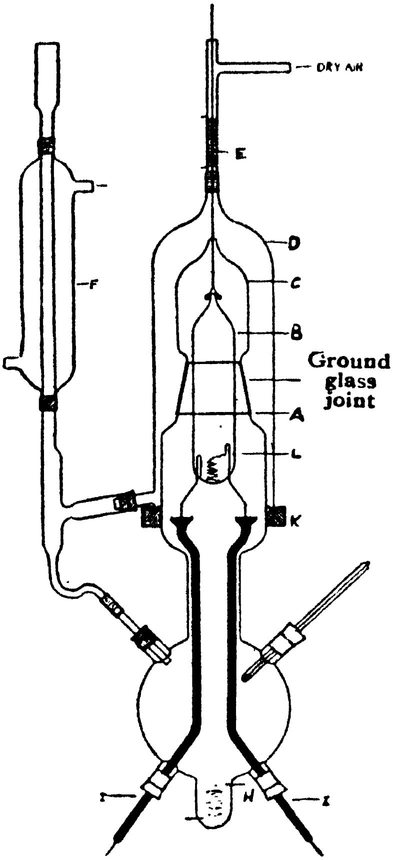

FIG. 15 (XXI^{3})
The vaporization apparatus of Mathews

The brass suspension wire, as it emerges from the outer vessel D, leads up through the centre of a coil of manganin resistance wire, encased in the glass ‘ chimney ’ E. By passing from 1 to 2 amperes of current through this heating-coil, condensation on the suspension wire is prevented. To prevent the escape of vapour from the ‘ chimney ’ E, a slow current of dry air is drawn into the apparatus by means of an aspirator bottle attached to the condenser F. An excess of dry air is passed into the ‘ chimney ’ under slight pressure, the excess not needed passing out at the top. A small standard Anschutz thermometer projecting into the boiler through a small tubulure is used to ascertain the temperature of vaporization.

The latent heat of vaporization of the liquid can be calculated from the formula,

$$Q = \frac{R \times T \times I^2}{W \times 4{\cdot}186}$$

where R = the resistance of the heating element
T = the time necessary to evaporate W grams of liquid
I = the current strength measured in amperes

The Technique of Glauque and Wiebe. In connexion with the study of the entropy of hydrogen chloride, these workers have made a careful examination of the heats of vaporization and their procedure with slight modifications has been adopted by many subsequent workers in this field. Their apparatus will therefore be described in some detail.[1] They employed two different types of calorimeter, one of glass and, later, one of gold. Two modifications of the glass calorimeter are shown in Fig. 16 (XXI^3). A thermocouple was placed in a long glass pocket. The pocket was filled with paraffin to improve thermal contact. A copper sheath shown at 3 was shrunk on to the upper portion of B. This acted as a radiation shield

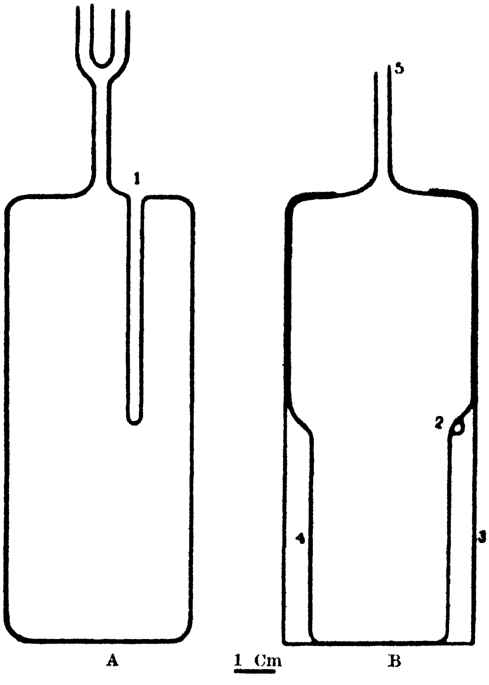

FIG. 16 (XXI^3)
Two modifications of the glass calorimeter of Glauque and Wiebe

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[1] *J. Amer. Chem. Soc.*, 1928, *50*, 104.

for the number thirty constantan wire heater, shown at 4, returning radiated heat to the calorimeter. A thermocouple was also attached to the sheath. To assist heat conduction a heavy sheet of platinum was coiled and placed in the interior of the glass calorimeter. Platinum was used because the better conducting gold was not immediately available. The inlet tube was closely wound with a heater of number thirty constantan wire which could be used to avoid the presence of solid within the tube. The inlet tube was sealed to the protective copper cylinder by Rose metal at point 5. The vapour pressures were measured by means of a manometer constructed of Pyrex glass tubing 2 cm. in diameter, and a cathetometer accurate to a few hundredths of a millimeter and with a precision of 0·01 mm. A trap filled with thin gold foil protected the calorimeter against distillation of mercury from the manometer. The copper-constanan thermocouple used for the vapour-pressure measurements was calibrated by means of the transition, melting- and boiling-point temperatures of hydrogen chloride.

The gold calorimeter is shown in Fig. 17 (XXI[3]). The cylindrical calorimeter A was made from gold sheet 0·75 mm. in thickness, with welded seams. The height was 12 cm. and the diameter 3·75 cm. Twelve radial vanes were placed inside to assist in attaining temperature equilibrium. The gases were introduced through a glass tube, of inside diameter about 2·5 mm., which was sealed to a short platinum tube, extending from the top of the calorimeter, by means of a lead and a cobalt-lead glass seal. The glass inlet tube was wound with a heater similar to that used in the glass calorimeter. A combined gold resistance thermometer heater[1] was used for measuring temperature intervals and introducing energy. The construction of the thermometer-heater was as follows: The sides of the gold calorimeter were coated with Bakelite lacquer and backed and dried for one week. The exterior was then coated with gold leaf to minimize radiation. For details of working, the original paper should be consulted.[2]

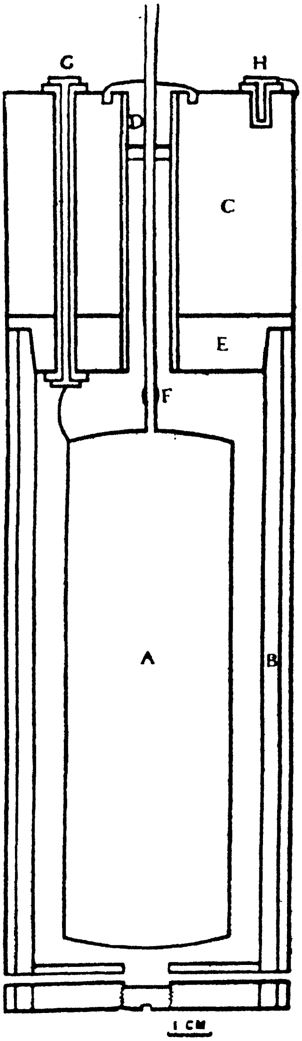

FIG. 17 (XXI[3])
The gold calorimeter of Glauque and Wiebe

Two methods of measurement were employed. The first was as follows: Two identical absorption-bulbs are attached to a line leading from the calorimeter in such a way that a three-way stop-cock controlled the flow of gas. The heating-current was turned on and the stop-cock opened into one of the absorption-bulbs. After several minutes a steady state was reached and the stop-cock was turned to direct the flow of gas into the other bulb. At the same time a calibrated stop-watch was started. The pressure remained constant to 1 mm. The second method was as follows: With one absorption-bulb on the line and the stop-cock closed, the warming rate was observed as in a heat-capacity determination. Then at a predetermined time the current was turned on, the stop-watch started, and shortly after this the stop-cock was opened. At the end the current was turned off and after the flow of gas had practically ceased the stop-cock was closed and the warming rate again taken.

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[1] Eucken, *Physik. Z.*, 1909, *10*, 586.

[2] *J. Amer. Chem. Soc.*, 1928, *50*, 101.

A Modified Method. A somewhat similar procedure to that of Glauque and Wiebe for the determination of heat of vaporization has been used by Aston and Messerly [1] except for the method of collecting the material after vaporization. A thin-walled glass bulb, connected to the line by a vaseline-sealed glass joint, was used for this purpose. It was immersed in a well-stirred bath of liquid and solid benzene, along with excess water, contained in a silvered Dewar flask. During vaporization the pressure remained constant to within a few millimetres except during the initial period required to build up the head necessary for heat transfer across the bulb, when it rose by about 20 mm. Before a measurement the calorimeter was brought to within a degree of the temperature of the bath of benzene containing solid frozen benzene.

The surroundings were at such a temperature as to be above that of the calorimeter at all times during the vaporization. The drift of the calorimeter was observed with a resistance thermometer until a sudden decrease in its value indicated that material had started to condense in the bulb. The heater was then turned on. The energy for the vaporization before the heater was turned on was calculated from the heat leak. At the end of the measurement the heater was shut off at a predetermined time and a stop-cock connecting the calorimeter to the rest of the line (manometer, condensing bulb, &c.) simultaneously closed. The drifts were followed until the calorimeter reached equilibrium.

An adiabatic calorimeter has been used by Aston and Eidinoff [2] to measure the temperature rise with this apparatus. There are no temperature gradients after equilibrium has been reached and a strain-free resistance thermometer heater can be used to measure the temperature rise. There are certain complications involved in the use of this apparatus, but its precision is high and it is accurate to 0·1 per cent for heats of vaporization measurements close to room temperature. The original paper should be consulted for details.[3]

The calorimeter also has application for other thermal measurements and a description of Aston and Eidinoff's calorimeter is given. The calorimeter (Fig. 18 (XXI[3])) is similar to that used by Southard and Brickwedds,[4] and the following is an explanation of the various numbers on the diagram: 1, calorimeter (volume 48 ml.); 2, thermometer well; 3, thermometer case (of platinum); 4, Pt-Rh (10 per cent) thermometer; 5, constantan thermometer ; 6, Rose metal filling; 7, platinum tube; 8, soft glass

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[1] *J. Amer. Chem. Soc.*, **1936**, *58*, **2354.**

[2] *Ibid.*, **1939**, *61*, **1533.**

[3] *Loc. cit.*

[4] *Ibid.*, **1933**, *55*, **4378.**

tube; 9, platinum thermometer supply wires; 10, platinum-cobalt glass seal; 11, radiation shield cylinder; 12, thermocouple guide tube (filled with paraffin); 13, standard thermocouple junction; 14, difference thermocouples; 15, couple support (glass tube); 16, brass screws; 17, radiation shield top; 18, Wood's metal thermal contact; 19, platinum tube; 20, difference thermocouple well (detachable paraffin-filled lug); 21, partial thermal insulation (silk gasket); 22, radiation shield bottom; 23, radiation trap; 24, 2-mm. hole for evacuation; 25, thermocouple junction; 26, 650 grams lead filling for 27; 27, copper case of massive ring, 750 grams of copper; 28, eye-bolts; 29, cord; 30, copper ring; 31, eye-bolt; 32, enamelled copper wires; 33, Wood's metal contact; 34, bakelite; 35, holes filled with paraffin; 36, thermocouple wires and insulated platinum potential leads; 37, thermocouple junction; 38, inner lead block, 1,150 grams lead; 39, hardwood pegs (wedge-shaped section); 40, pointed hardwood pegs; 41, thermocouple junction; 42, copper radiation shield; 43, Wood's metal contact of 44 with 8; 44, copper tube radiation shield; 45, copper lugs; 46, copper tube radiation shield; 47, copper lugs; 48, monel cryostat container; 49, glass tube guides for supply wires; 50, coiled wires and thermocouple; 51, paraffin-filled trough; 52, thermocouple junction; 53, first filling-tube thermo-

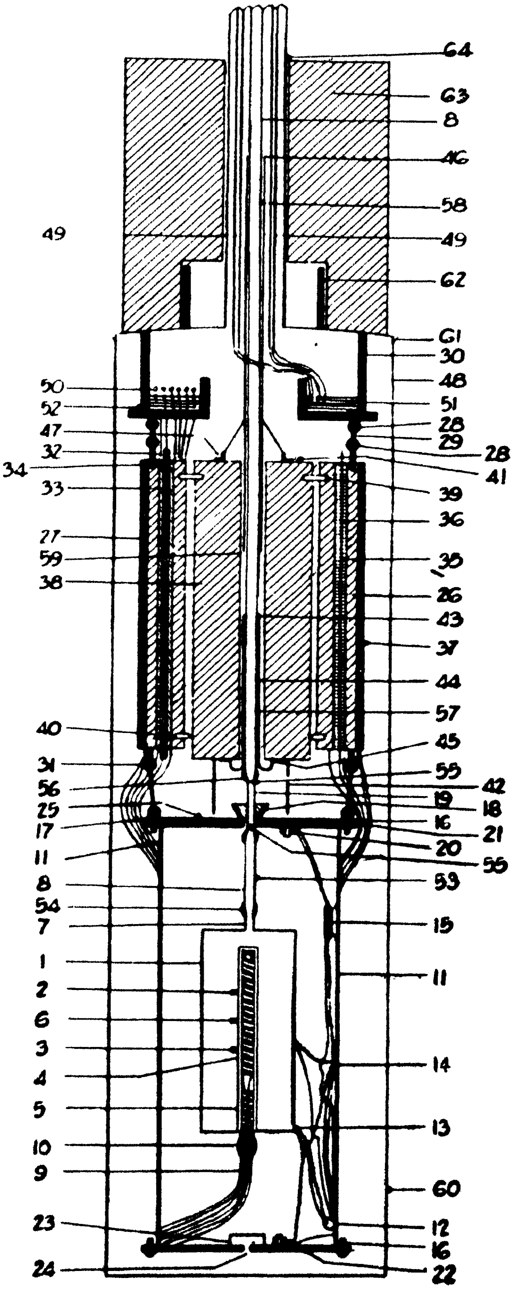

FIG. 18 (XXI³)
The calorimeter of Aston and Eidinoff

couple; 54, platinum-cobalt glass seal; 55, platinum radiation shields; 56, platinum-cobalt glass seal; 57, second filling-tube thermocouple; 58, third filling-tube thermocouple; 59, end of copper tube radiation shield; 60, thermocouple junction; 61, soft-soldered joint; 62, copper tube; 63, lead block (8,500 grams lead); 64, thermocouple junction.

The entire apparatus is suspended inside a large Dewar tube which fits inside a monel case with a cover. The apparatus is cooled by liquid air or hydrogen which is blown into the tube through a vacuum-jacketed transfer tube.

Using the above methods Aston, Eidinoff, and Forster[1] have determined the heat of fusion and the heat of vaporization of dimethylamine and the following record from their paper gives a good idea of the accuracy of this determination.

Table 1 gives the heat of fusion and Table 2 the heat of vaporization of dimethylamine.

TABLE 1

HEAT OF FUSION OF DIMETHYLAMINE

Mol. wt., 45·085; 0·66388 mole; melting-point, 180·97° K.

Temp. interval ° K.	Corr. heat input cal./mole	$\int C_p dT$ cal./mole	Pre-melting cal./mole	ΔH, cal./mole
174·871–185·932	1,751·9	332·8	0·6	1,419·7
174·774–184·736	1,711·9	292·2	0·5	1,420·2
172·079–185·489	1,806·6	386·5	0·3	1,420·4
			Mean . .	1,420·1 ± 0·5

TABLE 2

HEAT OF VAPORIZATION OF DIMETHYLAMINE

Mol. wt., 45·085; boiling-point, 280·04° K.

Moles vaporized	Mean temp. of vaporization ° K.	Total input cal./mole	Cal./mole	Ideal at 280·04 cal./mole	Real at 280·04 cal./mole
0·04270 *	278·71	7,176	849	6,352	6,302
0·11919	279·17	6,821	473	6,381	6,331
0·12539	278·95	6,682	328	6,383	6,333
0·11252	278·72	6,812	460	6,377	6,327
			Average of last three †		6,330 ± 3

* Due to the small sample a large error can arise from the uncertainty in the correction for the vapour in the lines. This result was therefore excluded from the average.

† Calculated value at 1 atmosphere is 6,408 calories.

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[1] *J. Amer. Chem. Soc.,* 1939, *61,* 1540.

During the vaporizations the pressure was held constant by having the condensation bulb immersed in a cryostat consisting of a well-stirred benzene ice-mixture with excess water. The benzene (thiophene-free) was purified by several crystallizations. In this way a bath was obtained with a constant and reproducible temperature.

Specific Heat

Micro-methods (*see* Vol. I, p. 445). To determine the specific heat of certain alloys or of rare metals it is convenient to have a method in which the examination can be carried out on a small sample, e.g. with a fine wire. The heat capacity of such a type of wire has been carried out by Kurrelmeyer, Mais, and Green [1] as well as by other workers.[2] The former workers adopt the following procedure. A wire enclosed in an evacuated tube is placed in one arm of a Wheatstone bridge and brought to the temperature at which its heat capacity is to be determined. With the bridge balanced, galvanometer key closed, and battery key opened, a charged condenser is connected across the battery terminals of the bridge. The heat capacity is evaluated from the resulting ballistic deflection. In an alternative procedure, the bridge is initially unbalanced so that discharge of the condenser gives zero deflection. The method has been tested on pure platinum in the neighbourhood of room temperature. The overall accuracy is estimated at 0·5 per cent.

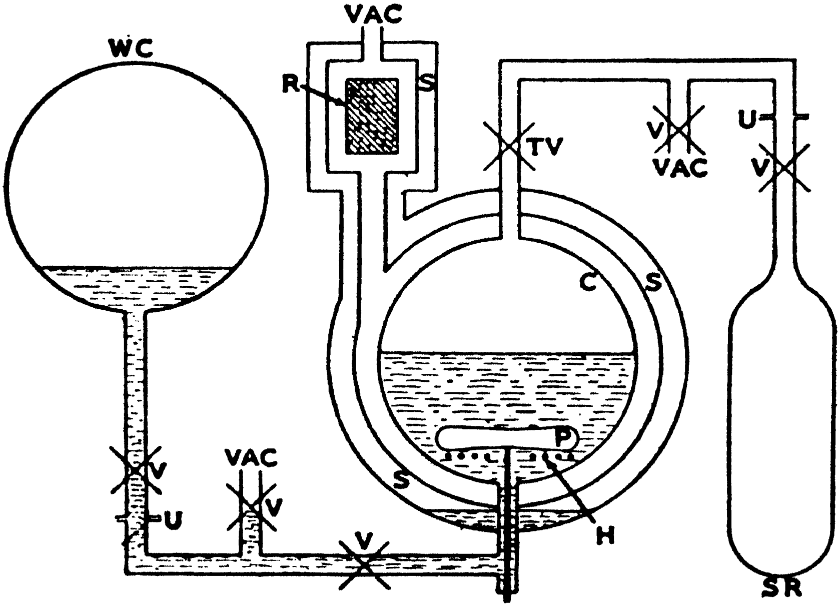

FIG. 19 (XXI³)
Schematic diagram of calorimeter of Osborne, Stimson, and Ginnings

Specific Heat of Water (*see* Vol. I, p. 445.4). The essential features of the calorimeter employed by Osborne, Stimson, and Ginnings, may be explained by reference to a schematic diagram (Fig. 19 (XXI³)), which shows the metal calorimeter shell C, containing a water sample ; an electric heater H ; and a water-circulating pump P. This shell is supported within an evacuated space which is surrounded by a controlled bath of saturated water vapour, which shields it against heat exchange with the surroundings. Provision is made for the introduction of a water sample from the water container WC into the calorimeter, or the withdrawal of saturated vapour through the throttle valve TV into the glass receiver SR. The calorimeter and flow lines may be evacuated through lines VAC. The reference block R provides a temperature datum determined by a platinum resistance thermometer. Auxiliary thermo-elements are used for measuring temperatures on the calorimeter shell and its surroundings, relative to this datum. The reference block is located in an enclosure surrounded by an extension of the steam-bath. The values of specific heat have been compared with values from several important researches by both the mechanical and the electrical method. This comparison shows a more satisfactory accord of the present results with the results of Rowland, of Laby and Hercus, and of Jaeger and von Steinwehr, than with those of Callendar and Barnes.

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[1] *Phys. Rev.*, 1941, *59*, 921; *Rev. of Sci. Inst.*, 1943, *14*, 349.

[2] Corbino, *Physik. Zeit.*, 1912, *13*, 375; Worthing, *Phys. Rev.*, 1918, *12*, 199.

References to all these authors in connexion with their work on heat capacities of liquids is given in the author's paper.[1]

Specific Heats of Certain Gases over Wide Ranges of Pressure and Temperatures. A wide study of the variations of the specific heats of 8 gases with temperature and pressure has been made by Ellenwood, Kulik, and Gay.[2] Their original paper gives detailed curves for the different gases and a good bibliography of the literature on this subject. One Table from the paper is given here giving some examples of the effect of pressure and temperature on the specific heats of gases.

Gas	Temp., ° F.	Pressure range, lb./in.², Abs.	Range of *Cp* B.Th.U./lb.-mole F	Percentage Increase in *Cp* due to pressure
Air	500	0–15,000	7·18– 8·39	16·87
	1,500	0–15,000	7·97– 8·39	5·33
Carbon dioxide CO_2 .	500	0–10,000	10·85–20·20	86·18
	1,500	0–10,000	13·15–14·90	13·31
Carbon monoxide CO .	500	0–10,000	7·17– 8·58	19·65
	1,500	0–10,000	8·05– 8·36	3·85
Ethylene C_2H_4 . . .	500	0–10,000	15·40–22·70	47·40
	1,500	0–10,000	23·12–24·40	5·54
Hydrogen H_2. . . .	500	0–10,000	7·00– 7·12	1·72
	1,500	0–10,000	7·30– 7·37	0·96
Methane CH_4. . . .	500	0–10,000	11·4 –13·58	19·14
	1,500	0–10,000	18·05–18·53	2·66
Nitrogen N_2	500	0–10,000	7·10– 8·08	13·85
	1,500	0–10,000	7·94– 8·20	3·28
Oxygen O_2	500	0–10,000	7·52–10·18	35·37
	1,500	0–10,000	8·44– 8·79	4·15

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[1] *Bureau of Standards J. of Research,* 1939, *23,* 197.

[2] *Cornell Univ. Eng. Expt. Station Bulletin No. 30,* 1943.

SECTION 7: EVAPORATIVE DISTILLATION

(*See* Vol. II, p. 103)

Practical Applications. The oils from the liver of certain fish constitute a source of vitamin A. The crude oils contain small amounts of valuable vitamins. Molecular distillation has afforded a method for removing the constituents causing unpleasant taste and odour and of concentrating the vitamins in a stable form. On subjecting the oils to molecular distillation, the primary fractions to distil contain the free fatty acids and the constituents responsible for the unpleasant taste and odour. Vitamin A, in its ester form, is found to concentrate in the next fractions, constituting 3 to 5 per cent of the original oil. These fractions also contain some vitamin D together with sterols and natural antioxidants. The concentrate of the vitamin A esters has a high stability, a uniform colour and clarity, and a high biological activity.[1]

The boiling-point, which is a criterion both of the identity and purity of volatile organic substances, has no direct analogy in molecular distillation. Hickman[2] has, however, shown that it is possible to systematize the course of molecular distillation so that a property of the constituents of the liquid, in terms of their relative heats of evaporation, and the relative purity of the single substances analogous to the boiling-point, may be measured. Hickman's method consists in the determination of the '*elimination curve*' for the specific substance. The theory of the elimination curve is based on the assumption that when a solution of a volatile component in a much less volatile liquid is passed through a still, the quantity of the volatile component evaporated at any moment will be proportional to its mole-concentration in the main bulk of the solution. To determine the elimination curve, a solution of a volatile component X in a much less volatile component Y is passed repeatedly through the still at a constant rate, the temperature being raised by a definite increment at each cycle. If the fractions are collected at each temperature and the total amount of component X in each fraction is plotted against the temperature, a symmetrical curve of the shape shown in Fig. 20 (XXI^3) is obtained, provided the temperature increments are small and the rate of circulation is slow. The curve has a maximum on the temperature axis which is characteristic of the given volatile component. The maximum of the curve may be located with an accuracy of ± 1° and is as definite a characteristic as the boiling-point.

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[1] Howat, *Chemical Age*, 1939; Burch, van Dyck, Fawcett, Burrows, Jewell, Mead, and Phillips, *J. Soc. Chem.*, Industry Symposium, 1939, *58*, 39. We are indebted to Mr. G. Burrows for reprints of papers contributed by the research staff of Metropolitan Vickers Electric Co. Ltd., to this symposium.

[2] *Ind. Eng. Chem.*, 1937, *29*, 968.

Both vitamin A and D complexes occur together in most fish-liver oils. In molecular distillation of these oils, vitamin A complex, the more volatile fraction, distils off at a considerably lower temperature than the vitamin D complex, the same relationship holding true in the case of the esters of the two types. Different fractions of the latter vitamin complex referred to as D_2, D_3, and D_4, may be obtained by irradiation of ergosterol, 7-dehydrocholesterol, and 22-dehydroergosterol respectively. The liver oils of different species of fish were found to have unequal antirachitic properties by carrying out biological assays on them, the experiments confirming the existence of more than one kind of vitamin D in the oils. Hickman[1] showed that the elimination curve for vitamin D was of unsymmetrical shape, proving a mixture of antirachitic substances of a varied distillability. On molecular distillation of pure calciferol an elimination curve of uniform shape is obtained.

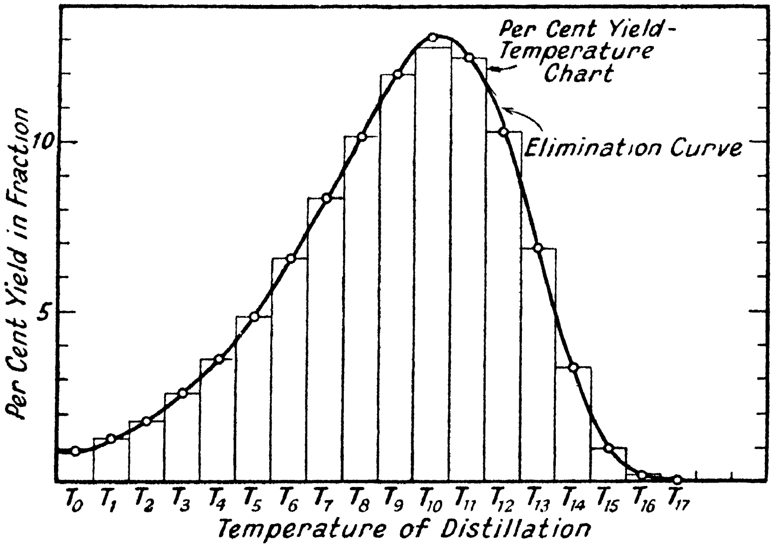

FIG. 20 (XXI[8])
Hickman's elimination curve

Separation of Mercury Isotopes. Two serious disadvantages associated with molecular distillation are (*a*) the low thermal efficiency, and (*b*) the poor fractionation obtained. The most serious cause of the low thermal efficiency is the high radiation loss amounting to no less than 60 per cent of the total heat supplied while the heat directly employed for distillation is only about 9 per cent of the total.

In molecular distillation in the absence of ebullition, evaporation can only occur from the surface of the liquid film. The fractionating power of the still is thus reduced. The outer layers become impoverished in the more volatile constituents so that the distillate received thereafter contains a high concentration of the less-volatile constituents, while the undistilled residue leaving the evaporator contains volatile constituents which have had no opportunity to evaporate. One of the earliest applications of molecular distillation is due to Brønsted and Hevesy,[1] who attempted a separation of the isotopes of mercury by fractionating a mixture of the light and heavy isotopes. The mixture of light and heavy mercury was placed in the spaces between the outer and inner flask of the Dewar vessel (Fig. 21 (XXI³)), S being thoroughly evacuated by means of a vacuum pump and the inner vessel A filled with liquid air. The mercury is evaporated

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[1] *Ind. Eng. Chem.*, 1937, *29*, 968.

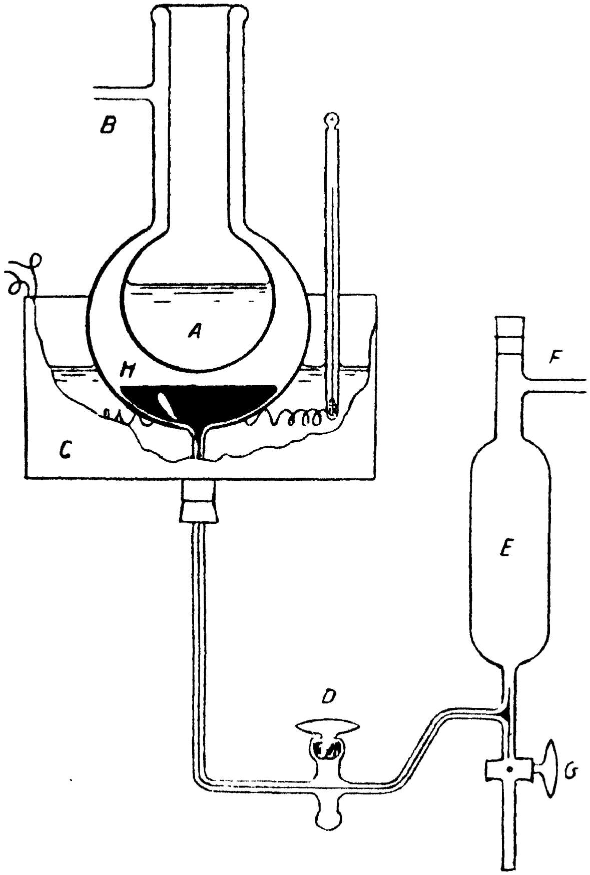

FIG. 21 (XXI³)
Molecular distillation apparatus of Bronsted and Hevesy

by surrounding the outer flask with an oilbath at about 40°–60°. After a suitable portion of the mercury is evaporated the remaining undistilled 'heavier' portion is removed by opening the stop-cock G. The lighter mercury which condensed on the surface of A is melted by evaporating the liquid air and removed in the same way as the heavier mercury. The operation is repeated until large distilled (D_1) and residual fractions (R_1) are obtained.

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[1] *Phil. Mag.*, 1922, *43*, 30.

In order to obtain heavy mercury, R_1 was submitted to a similar treatment as the original material and a residue (R_2) and distillate (R_1D_1) were obtained. By proceeding in the same manner and continuously decreasing remainder volumes (R_3, R_4 . . .) mercury of continuously increasing density was obtained. As seen from Table I (Brønsted and Hevesy) the density of the R fractions increase gradually as the original volume increases.

TABLE I

Fraction	Volume	Density	Fraction	Volume	Density
R_1	2,062	—	R_{10}	185	—
R_2	1,602	1·000016	R_{11}	150	—
R_3	1,283	—	R_{12}	128	1·000079
R_4	1,030	1·000024	R_{13}	42	—
R_5	791	—	R_{14}	10·3	1·000134
R_6	585	1·000034	R_{15}	5·5	1·000153
R_7	489	—	R_{16}	1·1	—
R_8	382	1·000053	R_{17}	0·5	—
R_9	268	—	R_{18}	0·2	1·000230

In order to obtain lighter mercury, D_1 is submitted to a further distillation and thus separated into a distillate D_2 and a residue D_1R_1 ; D_2 is treated in the same manner, and so on. Results showing in the continual decrease in density of the D fraction with decrease in volume is shown in Table II (Brønsted and Hevesy).

TABLE II

Fraction	Volume	Density	Fraction	Volume	Density
D_1	642	0·999977	D_8	2·3	0·999824
D_2	154	0·999953	D_9	0·9	0·999779
D_3	50	0·999933	D_{10}	0·7	—
D_4	13·5	0·999911	D_{11}	0·55	—
D_5	3·3	0·999881	D_{12}	0·5	—
D_6	7·0	0·999874	D_{13}	0·4	—
D_7	3·9	—	D_{14}	0·2	0·99974

The partial separation achieved is shown by the density measurements. The density difference found between the heaviest and lightest mercury amounted to 0·49 per cent corresponding to a difference of 0·1 unit in the element weight of mercury.

Fractionating Molecular Still. In molecular distillation, a type of fractionating column dependent upon the establishment of equilibrium between liquid and vapour obviously cannot be employed. In the falling-film type of molecular still, fractionation is achieved through passage of the distilland over the heating surface maintained at a definite temperature ; the maximum theoretical fractionation which can result in this way is equivalent to one perfect plate. To attain further fractionation, complex arrangements of combinations of still units designed to simulate the performance of fractionating columns have been employed.

A simple apparatus for multiple distillation which retains the condition for molecular distillation has been described by Wollner, Matchett, and Levine.[1] This is accomplished by providing within a single unit a series of communicating stages of distilling and condensing surfaces. As in the simple still, distillate from an initial stage is condensed on the roof of the still and engaged by a trough during its downward flow. Instead of being removed from the still, however, the distillate is directed by the troughs to a succeeding heating surface, located at a higher level than the preceding one. Here the more readily distilled portions are again preferentially evaporated, and again carried to the next stage. While the more volatile material progressively advances, the less-volatile material continuously regresses on the floor of the still toward ‘ rear-ward ’ heating surfaces. By applying heat in graduated amounts to the several sections of the still, with the greater amounts applied at the initial stages, the desired rate of distillation and ratio of reflux may be maintained.

The heating areas are defined by means of transverse ridges on the floor of the still, which act as dams checking the rear-ward flow of liquid and causing it to form shallow pools. The troughs are so located in relation to the pools as to engage distillate from each pool and conduct it to the succeeding pool. Liquid in each area is constantly replenished both by distillate from preceding areas, conveyed by the troughs, and by reflux from the superiorly located areas. The constant rear-ward flow of liquid along the heating surface and the merging of the counterflowing distillate and distilland at each stage serve to agitate and continuously renew the surface of the distilland.

The several heating areas are not distinct ; a continuous film of liquid covers the entire floor of the still, thereby providing the large distillation surface which is important in molecular distillation. The condensing areas on the roof of the still are, however, essentially distinct, each stage being the area between successive troughs. Material evaporated from any point on the heating surface is condensed on the surface immediately above it, and is necessarily carried to a forward point for redistillation.

The uppermost trough leads directly to a take-off tube, through which the distillate is conveyed to the receiver system. The still is connected to the usual high-vacuum system, in which operating pressures of 10^{-4} mm. of mercury or less are maintained. For further details and diagrams see original paper.[2]

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[1] *Ind. Eng. Chem. Anal.*, 1944, *16*, 529.

[2] *Ibid.*

SECTION 8: HYDROGEN-ION CONCENTRATION INDICATORS

Universal Indicators. These contain two or more acid-base indicators and are used to measure the *p*H value of a solution over a considerable range. Such a mixture acts as a single indicator with several stages of ionization, each associated with a change in hue: in general, the hues of the solution follow those of the spectrum in being red with acids and passing to blue or purple.

A number of such mixtures have been proposed and several commercial products are available.

Some of the proposed mixtures are given in Table A.

TABLE A

STOCK SOLUTIONS

(mg. per 100 ml. solvent)

Mixture	Kolthoff	Van Urk 1	Van Urk 2	Vanderburg	Smith	Bogen
Alcohol	95%	70%	70%	75%	95%	100%
Stock solution added to 50-ml. buffer .	0·8 ml.	0·5 ml.	0·25 ml.	0·5 ml.	0·5 ml.	0·25 ml.
*p*H range	3–12	3–11·5	2–12	2–10	4–10	2–10
Thymol-blue . . .	—	—	—	5	—	100
Tropaeolin . . .	—	—	70	—	—	—
Dimethyl yellow . .	18·8	—	—	—	—	60
Methyl orange . .	—	100	100	—	—	—
Bromocresol green .	—	—	—	—	20	—
Methyl red . . .	6·3	40	80	25	—	40
p-nitro phenol . .	—	—	—	—	50	—
Bromo thymol blue .	25·0	400	400	60	—	80
Neutral red . . .	—	—	—	—	4·5	—
Naphthol phthalein .	—	320	500	—	—	—
Cresol phthalein . .	—	1,600	400	—	—	—
Phenol phthalein . .	25·0	500	500	60	600	20
Thymol phthalein .	25·0	—	—	—	—	—
Alizarin yellow R .	—	—	150	—	—	—

Smith's mixture changes from blue in acids through green to purple in bases: also at *p*H 8·0 it is green, at 8·5 almost colourless and at 8·9 is purple. The commercial products appear to resemble Bogen's formula in their behaviours.[1]

Mechanism of the Glass Electrode. The transference of electricity through glass under conditions approximately those under which the glass electrode works has been studied experimentally by Hangaard,[1] the interchange of sodium and hydrogen ions being determined. The theory of Horowitz [2] seems to be fairly in line with the experimental results. Horowitz assumes that the glass electrode works as a hydrogen electrode on account of the ability of the glass to exchange sodium ions for hydrogen ions.

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[1] Woods and Mellon, *J. Phys. Chem.*, 1941, *45*, 313.

The following picture can be given of what occurs when a fresh glass surface comes in contact with an acid, neutral, or very weakly basic solution (that is, within the range where the glass electrode acts only as a hydrogen electrode) : at first the glass will take up water and the sodium salt of silicic acid will dissociate under the influence of the water taken up, hydrogen ions at the same time being absorbed ; in other words, the sodium salt of the weak silicic acid is partially hydrolized at the surface by the water, forming in the surface layer a skeleton of silicic acid. Hydrogen ions react readily with this surface, which affords an easy entrance of the hydrogen ions into the glass. In the middle of the glass there is a layer of intact sodium salt. With the passage of feeble currents through the membrane during the compensation of the E.M.F. of the system, there will be a slight movement of the salt layer towards one side, depending on the direction of the current. This ' transport ' theoretically does not require the doing of any thermodynamic work.

This theory is in many respects an extension of that of Horowitz and of a theory given later by McInnes and Belcher in the following words :

> a simple assumption, and one which accounts for all the phenomena within the *p*H range in which the glass electrode functions quantitatively, is that the hydrogen ion or proton can pass the electrolyte-glass boundary at a lower potential than any other positive ion and that negative ions do not pass the boundary at all. This does not involve any assumptions as to the conduction in the glass. It is quite probable that other ions than hydrogen move in the body of the glass.

These authors also emphasize the importance of the water absorption. The absorption of water by glass causes a swelling of the surface which has been demonstrated interferometrically by Hubbard, Hamilton, and Flynn, who also showed that a corrosion of the surface occurs when the glass is immersed in solutions the *p*H values of which are 9 and higher.

Use of Glass Electrode in Solutions of high *p*H. The measurement under anaerobic conditions of the *p*H of liquids such as blood is facilitated by the use of a glass electrode built into an hypodermic syringe.[3] Small quantities (0·2 ml.) of liquid can be used, and the *p*H at 38° readily determined with an accuracy of ± 0·02 *p*H. As already mentioned, the use of the glass electrode is not advisable in alkaline solutions of *p*H greater than about 8, since the slight solubility of the glass in such alkaline solutions leads to deviations from the linear relation between electrode potential and *p*H. However, for cases where various factors—for example, the oxidation-reduction potential of the solution—compel its use, several methods have been devised for overcoming this disadvantage. Thus Mazal,[4] in determining a *p*H of approximately 12, first calibrates the electrode by immersion in glycine-sodium hydroxide buffer solutions of *p*H's 11 and 13, or 11·5 and 12·5 if greater accuracy is desired. Jordan,[1] from a study of the deviations from the linear relation in alkaline solutions containing Na, Li, K, Ca, Sr, Ba ions at different pH values and ionic concentrations, found the empirical equation

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[1] *J. Phys. Chem.*, 1941, *45*, 148.

[2] *Z. Physik*, 1923, *15*, 369.

[3] Horwitt, *Ind. Eng. Chem. Anal.*, 1939, *11*, 30 ; apparatus manufactured by Rascher and Betzhold Inc., Chicago, Ill.

[4] *Chem. Abs.*, 1941, *35*, 4661.

$$\log \Delta = \mathrm{A}p\mathrm{H} + \mathrm{B} \log m - \mathrm{C}$$

where Δ = deviation from true value
m = ionic concentration
and A, B, and C are constants.

In strongly acid solutions (pH 0·5 — 2·0) the electrode shows a hysteresis effect, and it is necessary to wait till a steady state has been reached if an accurate value is desired.[2] The same authors found that provided temperature equilibrium was ensured in all parts of the measuring system, the glass electrode gave results in a large number of solutions of pH varying from 0·8 to 9·2, which agreed within 0·03 pH unit with the values obtained with a hydrogen electrode in the same solution.

Instead of a potentiometer for use with glass electrode systems in the measurement of small resistances, an electronic voltmeter has advantages in certain cases. This is especially the case in the determination of potentials of electrode systems that have a resistance of 5,000 megohms or less. A continuous reading electronic voltmeter suitable for such work has been described by Penther, Rolfson, and Lynken.[3] It gives satisfactory measurements of the E.M.F. between the electrodes in electrometric determinations involving the use of high-resistance glass, &c., and the corresponding reference electrode. It is applicable to potentiometric determinations in non-aqueous as well as aqueous solutions and has no tendency to produce polarization to the electrode. It is also suitable for pH determinations.

A Quinhydrone Cell. Elliot and Kilpatrick [4] describe a quinhydrone cell which was used in the determination of the effect of substituents in the acid strength of benzoic acid in methyl alcohol solution. The cell is shown diagrammatically in Fig. 22 (XXI³).

The type of cell measured was

$$\mathrm{Au}\left\{\begin{array}{lllll} \mathrm{H.B} & 0{\cdot}005\ \mathrm{M} & & \mathrm{HX} & 0{\cdot}005\ \mathrm{M} \\ \mathrm{Li\ B} & 0{\cdot}005\ \mathrm{M} & \mathrm{LiCl} & \mathrm{Li\ X} & 0{\cdot}005\ \mathrm{M} \\ \mathrm{Li\ Cl} & 0{\cdot}045\ \mathrm{M} & 1{\cdot}00\ \mathrm{M} & \mathrm{Li\ Cl} & 0{\cdot}045\ \mathrm{M} \end{array}\right\}\mathrm{Au}$$

$$\begin{array}{ccc} \mathrm{A} & & \mathrm{B} \\ \text{QUINHYDRONE} & & \text{QUINHYDRONE} \\ \mathrm{I} & & \mathrm{II} \end{array}$$

In the cell diffusion of the salt bridge solution contained in A into that portion of the cell containing the buffers B is prevented by the coarsely ground plugs C. These plugs are firmly seated at the beginning of any series of experiments. The electrodes D consist of a number of turns of gold wire E which are connected to a metal cap F. The cell caps G, which hold the electrodes, are fitted to the body of the cell by means of the ground-glass joints H, and the electrodes are held in this cap by the ground-glass joints I. Nitrogen, saturated with the solvent vapour by means of the bubbler J, is passed through the two buffers. The nitrogen then passes from the cell through the escape vent L, and leaves the cell by way of the bubbler K.

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[1] *Trans. Farad. Soc.*, 1938, *34*, 1305–10.
[2] Kubllka and Mazal, *Chem. Abs.*, 1941, *35*, 4659.
[3] *Ind. Eng. Chem. Anal.*, 1941, *13*, 831.
[4] *J. Phys. Chem.*, 1941, *45*, 454.

As can be seen from the figure, two electrodes are immersed in each buffer, affording four possible electrode combinations. This makes the detection of a poisoned electrode a simple matter. The method used in cleaning the electrodes was as follows: The electrodes are rinsed in tap water and then placed in warm cleaning solution (40°) for 15 min. After being rinsed in water containing a little ammonia, they are thoroughly rinsed with distilled water, wiped with an absorbent tissue, and stored in the solvent to be used. Before use they are carefully wiped and immediately placed in the buffer solution to be measured. Since the cells had a high resistance (10^{-7} ohms) a thermionic amplifier was used, together with a potentiometer and suitable galvanometer. The cell was used in an oil thermostat electrically controlled at 25° to 0·1°.

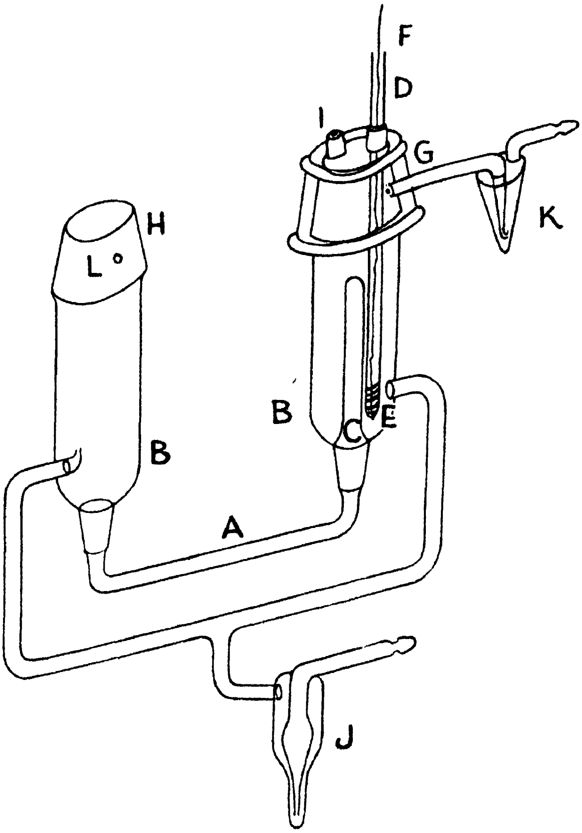

FIG. 22 (XXI')
A quinhydrone cell

To carry out a measurement the solution for the salt bridge was pipetted into the cell, the plugs placed in position, and the bridge solution allowed to come to thermal equilibrium in the thermostat. The plugs were then firmly seated, the excess solution removed, and, after rinsing with the buffer to be measured, approximately 5 ml. of the buffer was introduced; solid quinhydrone was added to each buffer, the electrodes were fitted in place, and nitrogen was passed through the buffers for 10 minutes. The E.M.F. of the cell was then measured, using all possible combinations of electrodes. It was found that there was no change of E.M.F. with time after 15 minutes and that small equal quantities of water in each buffer had no effect on the observed E.M.F.

Buffer Value, Buffer Power, or Buffer Effect.[1] In 1914 Koppel and Spiro expressed the buffer effect of a solution as

$$\frac{d(\mathrm{S} - \mathrm{S}_0)}{dp\mathrm{H}}$$

where S and S_0 represent the amounts of strong acid required to produce the change dpH when added to buffered and unbuffered solutions respectively. Since S_0 is so small as to be negligible this ratio becomes

$$\frac{d\mathrm{S}}{dp\mathrm{H}}$$

This aspect of buffer-activity does not appear to have received any further attention till 1922, when D. D. van Slyke of the Rockefeller Institute for Medical Research introduced the terms ‘ buffer value ’, ‘ buffer effect ’, and ‘ buffer power ’.[2] He worked out again, on lines similar to those of Koppel and Spiro, a mode of expressing quantitatively the relationship of buffer effect to the dissociation constant of the buffer and the reaction, and suggested, as a unit for the numerical expression of this effect, the ratio

$$\frac{d\mathrm{B}}{dp\mathrm{H}}$$

where dB is the increment, in gram-molecules per litre, of strong base B added to the buffer solution and dpH the resulting increment in pH. A solution may then be defined as having a buffer value 1 when the addition of 1 gram equivalent of strong acid or base to a litre will produce unit change in pH.

From the law of mass action the dissociation constant of a weak acid in dilute solution is given by the equation:

$$\mathrm{K}_a = \frac{[\mathrm{H}] \times [a]}{[\mathrm{H}a]}$$

where [H] is the concentration of hydrogen ions
[a] the concentration of anions
[Ha] the concentration of the undissociated acid

If a solution contains a salt Ba, as well as free acid, Henderson has shown that the equation may be expressed in the form

$$\mathrm{K}_a = \frac{[\mathrm{H}].\gamma_s.[\mathrm{B}a]}{[\mathrm{H}a]}$$

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[1] *Biochem. Z.*, 1914, *65*, 409.

[2] *J. Biol. Chem.*, 1922, *52*, 525.

where [B*a*] is the total concentration of the salt, both dissociated and undissociated, and γ_s is the fraction of [B*a*] which is dissociated.

Since the acid is only slightly and the salt highly dissociated the concentration of anion derived from the acid will be negligible compared with that derived from the salt and may therefore be included in $\gamma_s[\mathrm{B}a]$; we may then proceed as follows:

$$\mathrm{K}_a = \frac{[\mathrm{H}]\gamma_s[\mathrm{B}a]}{[\mathrm{H}a]}$$

$$\therefore\ \mathrm{K}_a[\mathrm{H}a] = [\mathrm{H}]\gamma_s[\mathrm{B}a]$$

But if

$$[\mathrm{H}a] + [\mathrm{B}a] = \mathrm{C}$$

$$[\mathrm{H}a] = \mathrm{C} - [\mathrm{B}a]$$

$$\therefore\ \mathrm{K}_a(\mathrm{C} - [\mathrm{B}a]) = [\mathrm{H}]\gamma_s[\mathrm{B}a]$$

$$\mathrm{K}_a\mathrm{C} - \mathrm{K}_a[\mathrm{B}a] = [\mathrm{H}]\gamma_s[\mathrm{B}a]$$

$$\therefore\ \mathrm{K}_a\mathrm{C} = [\mathrm{B}a](\mathrm{K}_a - \gamma_s[\mathrm{H}])$$

$$\therefore\ [\mathrm{B}a] = \frac{\mathrm{K}_a\mathrm{C}}{\mathrm{K}_a - \gamma_s[\mathrm{H}]}$$

$$= \frac{\dfrac{\mathrm{K}_a}{\gamma_s}.\mathrm{C}}{\dfrac{\mathrm{K}_a}{\gamma_s} - [\mathrm{H}]}$$

$$= \frac{\mathrm{K}_a{}'\mathrm{C}}{\mathrm{K}_a{}' + [\mathrm{H}]}$$

$$\therefore\ \frac{d[\mathrm{B}a]}{d[\mathrm{H}]} = -\frac{\mathrm{K}_a{}'\mathrm{C}}{(\mathrm{K}_a{}' + [\mathrm{H}])^2}$$

$$p\mathrm{H} = -\log[\mathrm{H}]$$

$$\therefore\ \frac{dp\mathrm{H}}{d[\mathrm{H}]} = -\frac{1}{[\mathrm{H}]\log_e^{10}} = -\frac{\log_{10}^{e}}{[\mathrm{H}]}$$

$$= -\frac{0{\cdot}4343}{[\mathrm{H}]}$$

$$\therefore\ \frac{d[\mathrm{B}a]}{d[\mathrm{H}]} \div \frac{dp\mathrm{H}}{d[\mathrm{H}]} = -\frac{\mathrm{K}_a{}'\mathrm{C}}{(\mathrm{K}_a{}' + [\mathrm{H}])^2} \div -\frac{0{\cdot}4343}{[\mathrm{H}]}$$

$$= \frac{[\mathrm{H}]\mathrm{K}_a{}'\mathrm{C}}{0{\cdot}4343(\mathrm{K}_a{}' + [\mathrm{H}])^2}$$

$$\therefore\ \frac{d[\mathrm{B}a]}{dp\mathrm{H}} = \frac{2{\cdot}3[\mathrm{H}]\mathrm{K}_a{}'\mathrm{C}}{(\mathrm{K}_a{}' + [\mathrm{H}])^2} \qquad . \quad . \quad . \quad \text{Equation A}$$

But from Henderson's equation

$$\mathrm{K}_a = \frac{[\mathrm{H}]\gamma_s[\mathrm{B}a]}{[\mathrm{H}a]}$$

$$\therefore\ \frac{\mathrm{K}_a}{\gamma_s} = \frac{[\mathrm{H}] \times [\mathrm{B}a]}{[\mathrm{H}a]}$$

$$\therefore\ \mathrm{K}_a{}' = \frac{[\mathrm{H}] \times [\mathrm{B}a]}{[\mathrm{H}a]}$$

From this

(1) . . . . $$K_a' = \frac{[H] \times (C - [Ha])}{[Ha]}$$

(2) . . . . $$K_a' = \frac{[H] \times [Ba]}{C - [Ba]}$$

from (1) $$K_a' \times [Ha] = [H] \times (C - [Ha])$$

$$\therefore\ [Ha] = \frac{[H] \times C}{K_a' + [H]}$$

from (2) $$K_a' \times C - K_a' \times [Ba] = [H] \times [Ba]$$

$$\therefore\ [Ba] = \frac{K_a'C}{K_a' + [H]}$$

but $$\frac{d[Ba]}{dpH} = \frac{2{\cdot}3[H].K_a'.C}{(K_a' + [H])^2}$$

$$\therefore\ \frac{d[Ba]}{dpH} = \frac{2{\cdot}3[Ba][Ha]}{C}$$

$$= \frac{2{\cdot}3[Ba][Ha]}{[Ha] + [Ba]} \quad . \quad . \quad \text{Equation B}$$

Buffer values, as defined above, calculated from the concentration of the acid and base constituents agree very well with those calculated from observations of actual changes in *p*H produced by the addition of strong acid or alkali.

The Point of Maximum Buffer Value. This buffer value $\frac{dB}{dpH}$ may be referred to as β

$$\beta = \frac{2{\cdot}3[H]K_a'C}{(K_a' + [H])^2}$$

dividing by C, the buffer value of a molecular solution will be given by

$$\beta_m = \frac{\beta}{C} = \frac{2{\cdot}3[H]K_a'}{(K_a' + [H])^2}$$

If we differentiate again

$$\frac{d\beta_m}{d[H]} = \frac{2{\cdot}3K_a'(K_a' + [H])^2 - 2{\cdot}3[H]K_a'(2K_a' + 2[H])}{(K_a' + [H])^4}$$

$$= 2{\cdot}3K_a'\frac{(K_a' + [H])^2 - [H](2K_a' + 2[H])}{(K_a' + [H])^4}$$

$$= 2{\cdot}3K_a'\frac{K_a'^2 - [H]^2}{(K_a' + [H])^4}$$

$$= 2{\cdot}3K_a'\frac{K_a' - [H]}{(K_a' + [H])^3}$$

$$\frac{dpH}{d[H]} = -\frac{0{\cdot}4343}{[H]} = -\frac{1}{2{\cdot}3[H]}$$

$$\therefore \frac{d\beta_m}{dp\mathrm{H}} = -\,2{\cdot}3^2[\mathrm{H}]\mathrm{K}_a'\frac{\mathrm{K}_a' - [\mathrm{H}]}{(\mathrm{K}_a' + [\mathrm{H}])^3}$$

$$= 2{\cdot}3^2[\mathrm{H}]\mathrm{K}_a'\frac{[\mathrm{H}] - \mathrm{K}_a'}{(\mathrm{K}_a' + [\mathrm{H}])^3}$$

when $[\mathrm{H}] = \mathrm{K}_a'$

$$\frac{d\beta_m}{dp\mathrm{H}} = 0$$

and $\frac{d\mathrm{B}}{e.dp\mathrm{H}}$ must be either a maximum or a minimum. From the curve showing the change of pH with added acid or base it is obvious that when $[\mathrm{B}a] = [\mathrm{H}a]$ the value of $\frac{d\mathrm{B}}{dp\mathrm{H}}$ is a maximum but

$$p\mathrm{H} = p\mathrm{K}_a' + \log\frac{[\mathrm{B}a]}{[\mathrm{H}a]}$$

from which $p\mathrm{H} = p\mathrm{K}_a'$ when $[\mathrm{B}a] = [\mathrm{H}a]$

$$\therefore\ \mathrm{H} = \mathrm{K}_a'$$

Hence both from equation A and equation B, the maximum buffering value will be given by

$$\frac{d[\mathrm{B}]}{\mathrm{C} \times dp\mathrm{H}} = \frac{2{\cdot}3[\mathrm{H}]\mathrm{K}_a'}{([\mathrm{H}] + \mathrm{K}_a')^2} = \frac{2{\cdot}3}{4} = 0{\cdot}575$$

$$\frac{d[\mathrm{B}]}{dp\mathrm{H}} = \frac{2{\cdot}3[\mathrm{H}a] \times [\mathrm{B}a]}{\mathrm{H}a + \mathrm{B}a}$$

in a molecular solution when $[\mathrm{H}a] = [\mathrm{B}a]$ each equals 0·5

$$\therefore \frac{d[\mathrm{B}]}{dp\mathrm{H}} = \frac{2{\cdot}3 \times 0{\cdot}5 \times 0{\cdot}5}{1} = 0{\cdot}575$$

SECTION 9: THE TESTING OF EXPLOSIVES

The stability of explosives is generally judged by tests of a physico-chemical or physical nature. This applies especially to storage trials at ordinary temperatures or under warm conditions. Such tests investigate whether alterations have taken place in physical properties, e.g. hardening, conglomeration, exudation, absorption of moisture, and in chemical properties, e.g. changes due to increased chemical reactions. A summary of these and related tests is given below.[1]

Density. The density of gunpowders and similar powders may be obtained by the methods given in Vol. I, Chap. XII. The density of blasting explosives in cartridge form may be estimated by weighing and measuring the cartridges. Another approximate method is to measure the displacement of sand. A glass tube is filled with sand and weighed. It is then emptied and a weighed stick of the explosive is inserted. Sand is poured in until the tube is full. The sand is levelled off and the whole is weighed. The apparent density of the sand is determined separately in the same tube.

Tendency to Segregate. Mixed explosives may tend to separate to some extent into their ingredients by shaking or by alternations of moisture in the atmosphere. The effect of shaking may be determined by putting a quantity of the explosive into a wide-mouthed bottle, so that the bottle is partially filled. The bottle is corked and shaken in a mechanical shaker for an hour. The explosive is then examined for visible signs of segregation and separate portions may be taken out and examined for differences in ease of ignition, &c. The effect of moisture is ascertained by exposing a sample in a flat dish for alternate periods of 24 hours to moist and dry air and examining after a week for efflorescence of crystals.

Movement of nitroglycerine in a cartridge by gravitation is tested by keeping the cartridge in a vertical position for some weeks at 32°. Portions from the two ends are examined for nitroglycerine content before and after the test, which may be carried out in dry or moist air.

Exudation. This refers mainly to nitroglycerine explosives. Exudation is undesirable, as the liquid nitroglycerine which exudes may become exploded by friction or shock. The exudation can be measured by placing a cylinder of the explosive on porous paper in a warm oven and ascertaining the amount of liquid which sweats out. A typical explosive is taken as a control. In one particular test a cylinder is cut from the cartridge, such that the length is about equal to the diameter. The ends are cut flat and the cylinder is placed on a flat surface and secured by a pin. It is then kept at 30° to 33° for 6 days and nights. The cylinder must not decrease by more than a quarter of its height, and the upper surface must retain its flatness and the sharpness of its edges. Sometimes pressure is applied to facilitate the exudation, and centrifuging has also been applied. To test the exudation due to freezing, the cartridges are frozen and thawed three times. Exudation is also met with in nitro-compounds which form eutectic mixtures.

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[1] For more detailed accounts of such tests, *see* Reilly, *Explosives, Matches and Fireworks*, Gurney & Jackson, London, 1938.

Inflammability. A small sample of the explosive is filled into a glass or paper tube about 2 cm. in diameter. The exposed surface is smoothed, and a slow fuse is brought in contact with it and ignited, to ascertain whether the explosive inflames and whether it burns partially or completely. The test should be repeated on several samples. The ease of inflammation may also be measured by playing a small bunsen flame on to the explosive for a measured time, say 10 seconds. Considerable differences are observed between different explosives. Control samples of known explosives should be included for comparison. Another method is to fasten a small quantity of the explosive to the end of a pendulum which swings through a flame in such a way that the time can be measured.

If the explosive has withstood the test in which it is exposed to the flame from a slow fuse, it is further tested by dropping a portion of 0·5 gram into a red-hot iron basin 12 cm. in diameter. The quantity may be increased to 5 gram if no explosion occurs. The basin must be well cleaned after each test and should be frequently renewed; on the other hand, a new basin does not give quite normal results until it has been used once or twice.

In some cases, larger quantities of a pound or two are burnt in a wood fire to ascertain the degree of danger to which the explosive may give rise in case of fire. The observations should be made under precautions at a safe distance.

Ignition Temperature. This is usually determined by placing 0·1 gram of the explosive in a small test-tube, which is then corked and placed in a fusible metal bath at 100°. The temperature is raised 5° per minute until inflammation or explosion occurs. The quantity and rate of heating differ in different countries.

Sensitiveness to Shock and Friction. The sensitiveness to blows is measured by the falling weight test. The explosive must be finely divided and well dried. A small portion is spread in a thin layer on an anvil. A bolt rests on the explosive and a cylindrical weight is allowed to fall upon it from a measured height. If explosion occurs the test is repeated with a lower height of fall until the mean height is found at which explosion just occurs. A standard explosive which can be obtained in pure condition, such as picric acid, is taken as a control. Considerable difficulty has been met with in obtaining reproducible results. An improved method was introduced by Rotter[1] in which the results of each impact are evaluated, not by personal judgment but by a quantitative measurement of the gas produced by the decomposition of the explosive. A number of typical results are quoted by Robertson. The sensitiveness to friction may be tested qualitatively by rubbing a small portion of the explosive vigorously in an unglazed mortar with an unglazed pestle. A useful test is to strike a glancing blow with a mallet, the explosive being laid on anvils of different materials. Howell's [1] apparatus consists of a steel anvil with grooves to hold the explosive (7 gram), and a swinging shoe which is allowed to fall with a circular motion from various heights.

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[1] *Cf.* Robertson, *J. Chem. Soc.*, 1920, *117*, 16.

Lead Block Test. This is one of the oldest tests for the explosive power, and is still widely used. The explosive is fired in a cavity in a cylindrical lead block. The cavity becomes enlarged and the increase of volume is taken as a measure of the power. Standard conditions were laid down at the Fifth International Congress of Applied Chemistry. The lead block is cylindrical and is 200 mm. in height and 200 mm. in diameter. The cylindrical cavity is 125 mm. deep and 25 mm. in diameter. 10 grams of explosive wrapped in tinfoil is taken for the test, and tamped with sand. The charge is fired by a detonator, and the expansion is measured by finding the volume of water necessary to fill the cavity. The original capacity of the bore is deducted and allowance should be made for the expansion due to the detonator. The purity of the lead and the temperature of casting of the blocks affect the results to some extent. The significance of the test is dealt with by Naoum.[2]

Ballistic Pendulum. A heavy mortar is suspended from a bearing and a stemmed shot is fired into it from a steel gun. The degree to which the pendulum swings gives a measure of the energy imparted to it. The weight of the mortar and height of suspension differ in different countries, e.g. at Rotherham 5·025 tons at 92 in., in America 14·1 tons at 89·75 in. The gun is brought to a measured distance from the mortar and fired electrically. Charges of $\frac{1}{4}$ to $\frac{1}{2}$ lb. of explosive are used, and a standard explosive is taken for comparison.

In another method a heavy mortar, firing at an elevation of 30°, is used. The explosive is detonated by means of a slow fuse and propels a projectile weighing 15 kg. The distance to which this is thrown is measured.

Brisance Meter. In using this apparatus, the violence of the explosive effect is measured by the crushing of a metal cylinder. The explosive is detonated on a steel plate, covered by two lead disks for protection. The steel plate is 2 cm. thick, weighs 320 grams and is supported by a piston fitting into a hollow steel cylinder. The lower end of the piston rests on a copper cylinder supported by the steel base. The detonation of the explosive transmits a pressure through the piston to the copper cylinder, and crushes it to an extent which can be measured. The degree of crushing is used to compare the brisance of different explosives.

Rate of Burning. A description is given here of the method worked out by Taylor and Wark [3] for the determination of the rate of burning of propellants. The method has been in operation since 1930 and has proved to be both convenient and reliable in operation. The principal novel feature which distinguishes it from previous equipment [4] is the method of optically magnifying the extremely small movements of the pressure member (Petavel type), without any mirror or mechanical levers. This enables a very light, robust, short-time period gauge to be constructed which gives very high quality pressure-time traces capable of accurate measurement, and which for many purposes is as accurate as and much more convenient than piezo-electric gauge installations.

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[1] *U.S. Bureau of Mines, Tech. Paper*, 234.

[2] *Z. ges. Schiess- u. Sprengstoffw.*, 1932, *27*, 181, 229, 267.

[3] This description is from the *J. Sci. Inst.*, 1946, *23*, 115, and is published here with the permission of the authors. The Editor of the *Journal* has provided the electros for the related figures.

[4] Petavel, *Phil. Trans. A*, 1905, *205*, 357; Crow and Grimshaw, *Phil. Trans. A*, 1932, *230*, 39; Balfour, *Engineering*, 1932, *134*, 231.

The Closed Vessel. The closed vessel (Fig. 23 (XXI[3])) was made from a single ingot of Vibrac steel (tested up to 80 tons/sq. in.). It had been the usual practice to bore a closed vessel laterally in order to introduce a gas-release valve. This was avoided in the present design, and the gas-release valve was incorporated in the breech block or firing head (Fig. 24 (XXI[3])).

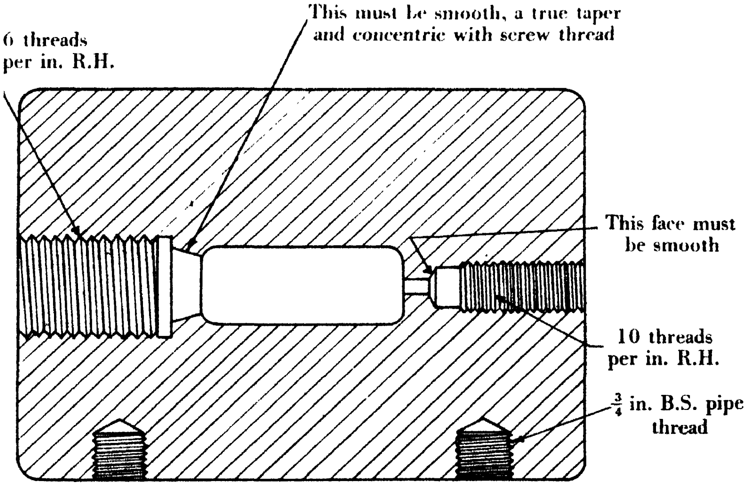
6 threads
per in. R.H.
This must be smooth, a true taper and concentric with screw thread
This face must be smooth
10 threads
per in. R.H.
$\frac{3}{4}$ in. B.S. pipe thread

FIG. 23 (XXI[3])
The closed vessel (quarter size)

The closed vessel is bored axially at both ends, the one end to take the breech and the other the pressure gauge. The breech closure is of the conical sealing type with a mild steel conical lining washer. The breech contains an insulated firing electrode and a gas-release valve as shown in Fig. 24 (XXI[3]).

The cavity of the vessel normally used is approximately cylindrical and of volume 121 ml. From the enclosure a $\frac{1}{2}$ in. deep hole, 0·3 in. diameter, leads to the gauge which is screwed into a $\frac{7}{8}$ in. diameter boring. The gauge plug is seated on to a conical seating, sealing being effected by means of a lens ring. This ring is a double convex lens or washer of specially heat-treated steel which is used for high-pressure couplings or sealing. The seatings for the lens ring may be plane or conical and are such that contact is made circumferentially between the lens ring surface and the seatings. The body of the vessel is mounted rigidly in an iron cradle mounted in a concrete block, in such a way that the axis is horizontal.

Pressure Gauge. The pressure gauge used is a modification of the rifle-pressure gauge.[1]

Mechanical pressure indicators usually comprise a pressure member which is put into a state of compression or flexure by the action of the pressure incident upon it. The magnitude of the compression or flexure is used as a measure of the pressure itself, and since the magnitude is small various methods are employed for its magnification and registration. These are usually mechanical and optical in nature and consist in constraining the pressure member in its motion to rotate a mirror suitably linked up to it.

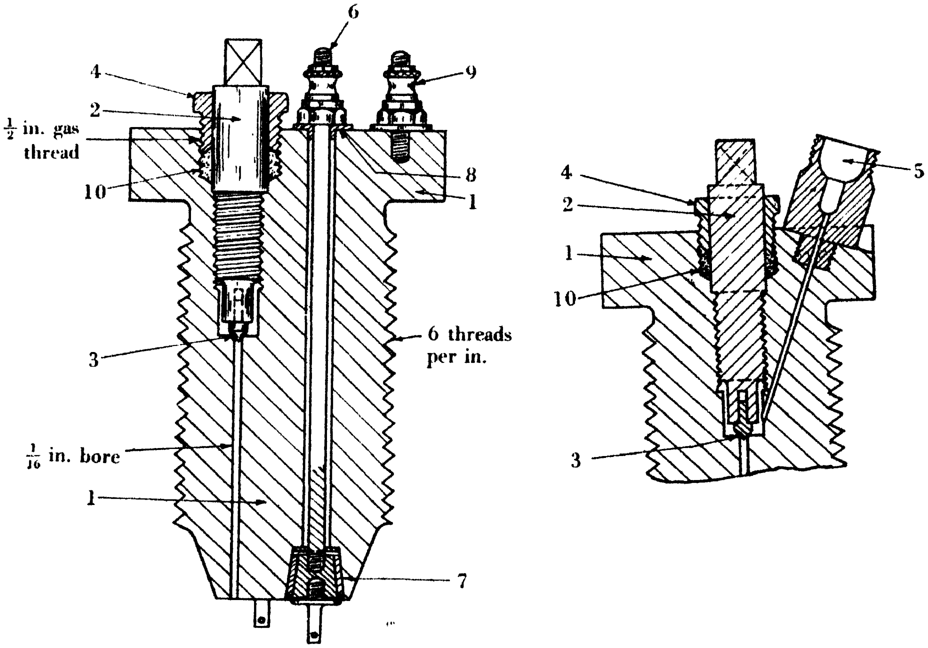

FIG. 24 (XXI[3])

The firing head (half size). (1) body; (2) valve spindle; (3) valve; (4) gland; (5) gas inlet; (6) electrode; (7) cone and washer; (8) washer; (9) terminal; (10) packing

The rotation of the mirror is arranged to be proportional to the motion of the pressure member which in turn is made to be proportional to the magnitude of the pressure operating. Of such a nature are the recording systems of the Petavel and Thring pressure gauges, and also the Webster and Thompson pressure indicator.[2]

Such methods of recording have attendant disadvantages. Where a pressure-time record of very rapidly changing pressure is required, the mass of the moving parts and the time period of the gauge must be cut down to minimum values. The recording system of mirror, mirror controls and coupling, reduces the natural frequency of the pressure member, and if this system is made excessively small in an attempt to reduce its mass, deformation of the system under the high working pressures usually ensues, thereby introducing changes in the ‘ zero ’ position of the mirror system or deviations from a linear pressure-movement law. Further, the natural time period of the recording system itself acts partly independently of the pressure member and causes perturbations. It is also impractical to reduce the time period of the mirror system to a value comparable with that of the pressure member, and, moreover, it is difficult to avoid play between the coupling of the pressure member and mirror whilst maintaining a sufficient flexibility of parts. These defects can and do play a part in all recording systems of pressure gauges.

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[1] *Game and Gun* (Technical Supplement), July 1933; *Nature*, Lond., 1932, *129*, 725.

[2] Petavel, *Phil. Trans. A*, 1905, *205*, 357; British Patent Specification 163,742. Webster and Thompson, *Proc. Nat. Acad. Sci.*, *Wash.*, 1919, *5*, 259; Crow and Grimshaw, *Phil. Trans. A*, 1932, *230*, 39.

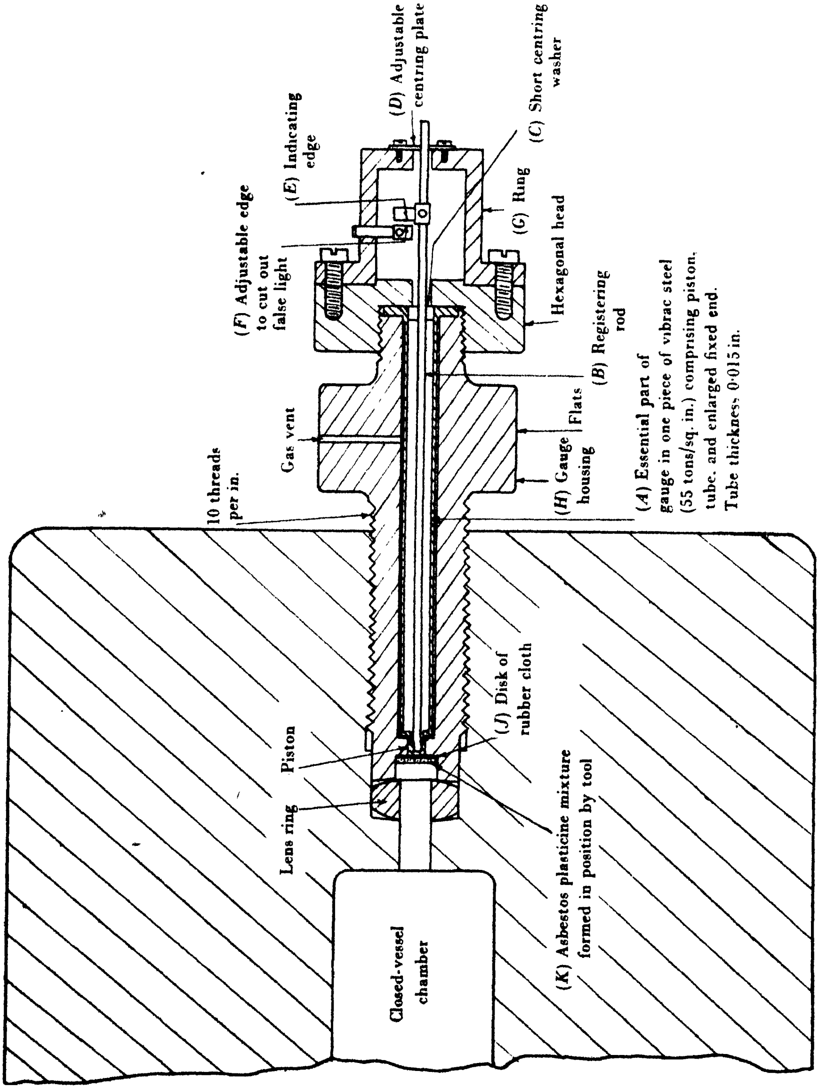
(D) Adjustable centring plate
(C) Short centring washer
(E) Indicating edge
(G) Ring
(F) Adjustable edge to cut out false light
Hexagonal head
(B) Registering rod
(A) Essential part of gauge in one piece of vibrac steel (55 tons/sq. in.) comprising piston, tube, and enlarged fixed end. Tube thickness 0·015 in.
Flats
Gas vent
(H) Gauge housing
10 threads per in.
(J) Disk of rubber cloth
Piston
Lens ring
(K) Asbestos plasticine mixture formed in position by tool
Closed-vessel chamber

FIG. 25 (XXI[3])
The pressure gauge (half size)

By recording the motion of the pressure member or gauge itself solely by means of optical enlargement and without using a rotating mirror or other similar device, the authors have overcome the difficulties mentioned above.

The movement of the pressure member is communicated to an operating or registering rod rigidly connected to the pressure member at the piston end of the gauge where the maximum movement takes place. The free end of the operating rod carries a piece of the edge of a new safety-razor blade at right angles to its longitudinal axis and direction of motion. By means of suitable illumination by light, an enlarged image or shadow picture of the razor edge is formed on the film of the camera used for photographing the records. Two magnifications have been used with the closed-vessel pressure gauge, the values being roughly × 120 and × 60. The enlarged image is concentrated in a direction normal to the long axis of the razor edge by means of a cylindrical lens, so that a linear image in the form of a black and white line is formed on the film of the camera.

The gauge (Fig. 25 (XXI^3)) is of the single steel-tube type having a piston at one end free to move; the parts are of Vibrac steel. When the gas pressure acts on the base of the piston, the tube is compressed by an amount proportional to the pressure, provided the elastic limit of the steel is not exceeded. The end remote from the piston is, of course, to all intents fixed. The movement of the piston is recorded by the optical method described below.

The chief feature of the present design is that, whereas earlier gauges consisted essentially of three main parts, namely, the tube proper, the piston, and the fixed end-piece remote from the piston, all three being joined together by pins, the working part is all in one piece of steel A, thus eliminating one source of error, namely, play at the joints. The piston end is short in order to restrict friction due to eccentricity. The registering rod B is screwed into the piston, as it was found to be impracticable to make this in one with the gauge proper. The registering rod is centred at the fixed end of the gauge by a short detachable piece C which may be removed before each assembly in order to check that the rod is concentric with the gauge. Transverse vibrations may be set up if this piece is omitted. The rod finally passes through the end-support carrying a thin centring plate D which is adjusted finally so that there is no load sideways on the rod. Friction due to the rod is thus reduced to a minimum. The indicating edge E is held by a screw to a small holder which is itself screwed to the registering rod. Close to this edge is a second adjustable edge F attached to the ring G; this serves to restrict unwanted light and improve definition.

The method of obturating the piston of the gauge is also shown in Fig. 25 (XXI^3). The base of the gauge housing H is opened out to a diameter of 0·4 in. as far as the base of the piston. A well-fitting circular disk J of rubber cloth is first placed at the base of the recess followed by a layer K of an asbestos-plasticine mixture weighing $\frac{1}{3}$ gram., which is then well formed by a good fitting tool. The piston of the gauge is lubricated by a small application of Arctic sperm oil. The obturation is renewed every seven shots. The system has been very satisfactory and free from gas leakage over several thousand shots, and is practically frictionless. The natural frequency of the gauge was measured and found to be just over 6,000 complete vibrations per second, which is high enough to deal with the pressure-time rises normally under investigation.

Optical Method and Apparatus for recording Gauge Movement. The optical system employed for enlarging and recording the very small motions of the razor edge attached to the operating rod of the gauge (maximum movement less than 0·02 in.) is essentially similar to that used for photographic registration with the Einthoven string galvanometer. A diagrammatic sketch of the set-up is shown in Fig. 26 (XXI^3). A reduced image of a Pointolite ball P (100 c.p.) is thrown by means of a lens L (double convex lens, 5 cm. focal length, diameter 5 cm.) and microscopic objective M_1 (Parachromatic $\frac{2}{3}$ in. focal length) upon the razor-edge indicator of the operating rod. The optical axis of the lens and objective system is normal to the razor-edge axis, and the image of the Pointolite ball is in the plane through the axis of the razor edge perpendicular to the optical axis. The strongly divergent light from the Pointolite image from the razor edge is collected by a second and similar objective M_2 so as to give a magnified image on the drum of the camera C. This magnified image consists of the Pointolite ball cut into two by the razor edge which gives a finely focused edge EE as shown in Fig. 27 (*a*) (XXI^3.) The magnified image is collected to a linear focus on the drum of the camera by the cylindrical lens L_1 (focal length $4\frac{1}{2}$ cm., aperture 1 cm., length 9 cm.). The linear image formed in this way consists of a black line sharply joining a line of light as shown in Fig. 27 (*b*) (XXI^3). When a deflexion of the gauge occurs it is recorded in the linear image as a motion of the line of light into the black line, for the motion of the needle is such that it exposes more of the Pointolite image when the gauge is deflected. The magnitude of this motion is directly proportional to the actual motion of the pressure member. The linear image falls upon a photographic film on a drum camera. A time scale from a 1,000 c/s tuning fork is registered on the film whilst it rotates. The axis of rotation of the drum camera is parallel to the direction of displacement of the pressure

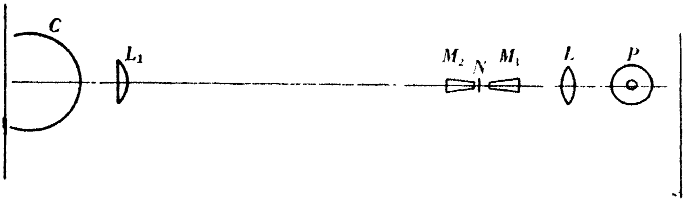

FIG. 26 (XXI^3)
Optical system for recording pressure changes

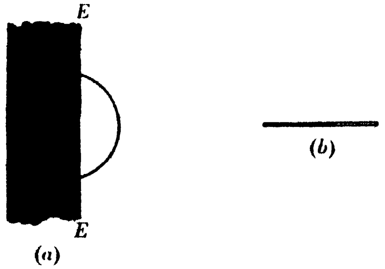

FIG. 27 (XXI^3)
Magnified image of razor edge

member. The camera exposure and firing of a round are synchronized in a manner that will be described later.

The optical parts are mounted on a 100 cm. optical bench (Zeiss) on saddle stands. The objectives are mounted on saddle stands fitted with microhorizontal adjustments. This set-up ensures accurate and rapid assembly of parts and delicacy of adjustment. The optical bench is rigidly fixed to the concrete mounting by means of iron clamps.

The Camera. The camera itself comprises a metal drum of 19·4 cm. diameter and 9·4 cm. height. It is mounted by iron brackets rigidly upon the wall of the test house with the axis horizontal, and in the plane of the axis of the closed-vessel gauge, and driven by an electric motor at a suitable speed, normally about 360 r.p.m., i.e. a film speed of 375 cm./sec. through a string belt. The adjustment of the film to the camera is of the slot and split-pin type.

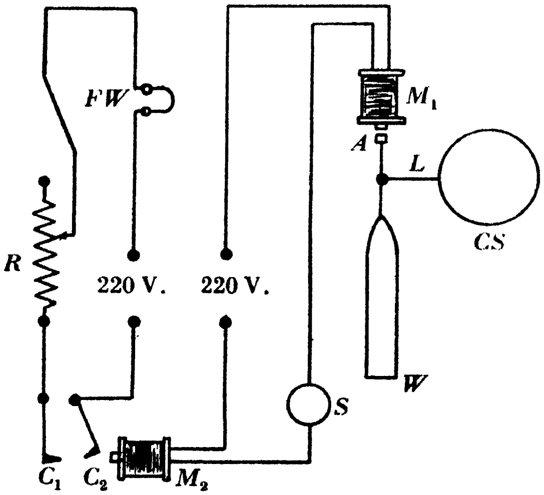

FIG. 28 (XXI^3)
Synchronizing circuit

Synchronization of Camera Opening and Firing. Fig. 28 (XXI^3) is a diagram of the firing circuit. The camera has a D.R.P. compound shutter CS, with set seconds speeds, which are the reciprocal of the following numbers: 1, 2, 5, 10, 25, 50, 75. (Alternatively a focal plane shutter is used.) It has a small armature A and a weight W attached to it as shown, in such a way that when the armature A is free, the fall of the weight W causes an exposure to take place. The armature A is supported by means of the electromagnet M_1 when it is energized. M_1 is connected in series with a firing switch key S, a relay M_2 and the 220 V d.c. mains. The relay M_2 is an Ericsson P.O. 1,000 Ω type relay to break two circuits. M_1 comprises the magnet from such a relay. When M_2 is energized it breaks the contacts C_1, C_2 and keeps them apart. These contacts are connected in series with an adjustable resistance R, the mains and the closed vessel terminals and firing wire FW. When the switch S is opened, M_1 and M_2 are de-energized, W begins to fall, and at a definite instant the camera shutter CS opens and remains open for a time, determined by the set speed. At the same time contact between C_1 and C_2 becomes established and the firing wire FW of the closed vessel is blown. By adjustment of the set speed, the contacts C_1, C_2, and the resistor R, the time at which the firing wire is blown, can be adjusted.

The closed vessel is filled with a mixture of one part of hydrogen and one of air (by volume) at a pressure of 2 atm.; this is exploded by the ignition of the firing wire FW. The powder charge has a small ($\frac{1}{4}$ gram) charge of dry gun-cotton placed around it, and the combined effect of the explosion of the gas and the gun-cotton ignites the powder charge uniformly over the surface.

The exact settings of the set speed of the shutter, of the contact C_1, C_2 and the resistor R are adjusted by trial and error until the pressure-time record is obtained in an exposure equivalent to one complete revolution of the camera.

Time Marking and Measurement of Records. Time marks on the film are produced by means of a light pencil trace from a small concave mirror mounted upon the armature of a balanced-armature type loud-speaker unit. The vibrations of the mirror are induced and controlled by means of a valve-operated tuning fork of 1,000 c/s, in conjunction with a valve amplifier.

The photographic records are measured up by means of a co-ordinate reading comparator.

Calibration of Closed Vessel Pressure Gauge. The closed-vessel pressure gauge was calibrated on an oil-pressure unit which gives pressures up to a maximum of 30 tons/sq. in. The gauge was set up precisely as when used for the closed vessel in a fitting coupled to an extension pipe connected to the oil-pressure unit. The whole fitting and extension pipe was filled with pure castor oil right up to the end of the gauge piston obturation. The oil pressure was read by means of a Schäffer and Budenberg gauge (dial reading type) reading in divisions of 20 kg./sq. cm. from zero to 5,000 kg./sq. cm.

In carrying out experiments, the speed of the camera was reduced to about 1 rev./hr. Pressure was applied by means of the pumps, and when a suitable pressure was attained in the oil press, the magnitude of the pressure was read on the dial gauge and simultaneously an exposure of the closed-vessel gauge camera was made. In this way readings were taken of both dial-gauge and closed-vessel gauge deflexions from about 0·1 ton/sq. in. up to 20 tons/sq. in. Since the gauge operates on the up-stroke only, it is unnecessary to calibrate it on falling pressure. The readings obtained by this method included a correction due to the pressure-pipe extension from the oil press to the closed-vessel pressure gauge. The magnitude of this correction was determined as a function of pressure by attaching an edge rigidly to the extension pipe and using this in a similar manner to the ordinary gauge for determining the extension for different pressures.

The calibration was linear up to about 20 tons/sq. in. The calibration of the gauge widely used at the present time is 8·87 tons/sq. in./cm. deflexion.

Experimental Method. In carrying out an experiment in the closed vessel, the charge, if tube or cord, is cut to lengths of 7·5 cm., the required amount is weighed out and a symmetrical bundle is made of the sticks, together with the small charge of dry gun-cotton, by tying them with a small amount of fine silk thread. The charge is put into a closed vessel which is then fastened up. After this the hydrogen for ignition is introduced into the vessel from a cylinder. Before firing, an exposure of the camera is made with the gauge undeflected. This exposure gives the base for the pressure-time record. The firing switch is then operated, the 'firing' gas is exploded and ignites the gun-cotton, and the flame uniformly ignites the powder charge. The firing switch also operates the electromagnetic control of the camera shutter, the camera operation is synchronized with the powder ignition.

Fig. 29 (XXI^3) gives examples of the type of pressure-time records obtained with the apparatus. The time marks are seen at the base of the records and represent 0·001 sec. from crest to crest.

Rate of Detonation. Two methods are in use. In the direct method, the time of detonation of a measured length of a column of explosive is determined. This necessitates the accurate measurement of very short time intervals, which is effected by means of a rapidly rotating drum fitted with a speed recorder. The column of explosive is fitted with wires at a fixed distance apart, generally 1 metre. The rupture of the wires gives rise to induction sparks, which give spots on the smoked surface of the drum. By measuring the distance between the spots, the rate of detonation can be calculated. The velocity depends upon the diameter of the train of explosive up to a limiting value, the degree of confinement, the density, and the method of initiation.

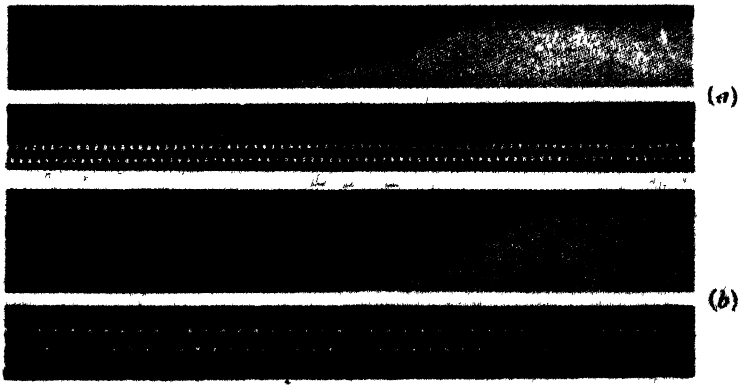

FIG. 29 (XXI^3)
Typical pressure-time curves at a loading density of 0·2 (a) for tubular propellant, (b) for cord propellant (half size)
1 cm = 8·87 tons/sq in on original

In Dautriche's method the explosive to be tested may be in cartridges or compressed into a tube A containing the high explosive, and a detonator is inserted at one end (Fig. 30 (XXI^3)). Two other detonators are inserted into the sides of the tube at a known distance apart, and connected to a loop of the detonating fuse. When the explosive is detonated the detonation is transmitted successively to the two ends of the detonating fuse, and the two waves meet at a point depending on the rates of detonation of the main explosive and of the explosive in the detonating fuse. The point at which the waves meet is ascertained by the indentation of a slab of lead P on which the detonating fuse lies.

The sensitiveness to detonation is determined by subjecting the explosive in its usual form (e.g. in cartridges) to the action of detonators of different intensities. These are fired electrically, and the effect on the explosive is observed.

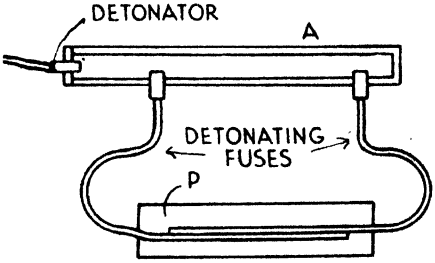

FIG. 30 (XXI^{3})
Schematic diagram of Dautriche's method of determining rate of detonation of an explosive

In order to ascertain the propagation of detonation, two cartridges are placed end to end on the ground at a certain distance apart, and one of them is detonated. By varying the distance it can be ascertained at what distance the first cartridge detonates the second.

Length and Duration of Flame. These are of importance in connexion with the ignition of fire-damp, &c. The measurements are made photographically. A sensitive film is fixed to a drum, which is rotated at a known speed, and the flame is photographed through a narrow slit in such a way that the height of the image shows the length of the flame and the breadth shows its duration.

Testing of Detonators. A review of the methods used for detonators is given by Kast and Haid.[1] The initiating action may be determined by the Esop and Wöhler tests in which the detonator is fired in contact with an explosive which has been partially deadened by the addition of an inert substance. Tests are also made to determine the limiting charge of a detonator composition, which just suffices to bring about detonation. In the 'Sand test' of the U.S.A. Bureau of Mines, a detonating charge is exploded in a mass of carefully graded sand and the degree of pulverization caused by the explosion is measured. In the 'Nail test' the detonator is attached by means of wire to a nail, the two being parallel and the lower end of the detonator being level with the centre of the nail. The power of the detonator is measured by the degree of bending of the nail. Standard nails must be used for the test.

The Trauzl test is sometimes used with a smaller lead block. The indentation of a lead plate is also frequently made use of.

The Rate of Decomposition of Detonators. The rates of decomposition of the two forms of lead azide crystals have been measured by Garner and Gomm.[2] These rates were measured by suspending the crystals in a platinum bucket in a Pyrex vessel surrounded by a furnace which was kept at temperatures ranging between 200° and 300°. The exploratory work was carried out with the α-azide, and several facts were observed, which determined the final design of the apparatus. The crystals often broke up into several fragments on heating, and the fracture was accompanied by the evolution of small volumes of gas. Reproducible results could not be

[1] *Z. Ger. Schiess. U. Sprengstopfer.*, 1924, *19*, 146.
[2] *J. Chem. Soc.*, 1931, 2127.

obtained until the crystal had been heated to a temperature higher than that at which it was desired to make measurements. The detonation temperature varied with the pressure of gas in the apparatus. It was thus necessary to bake out the apparatus thoroughly before an experiment.

Apparatus.—Two Pyrex reaction vessels were used (A and B, Fig. 31 (XXI³)), which were connected to a McLeod gauge M and through a phosphoric oxide tube to the pumps. These were surrounded by lagged furnaces, worked on constant voltage and capable of being raised and lowered. The furnaces and McLeod gauge were surrounded by wooden jackets to protect them from draughts. The temperature was measured by means of a copper-constantan thermocouple, which was inserted into a vertical tube in the reaction vessel. The platinum bucket containing a crystal was suspended by thin platinum wire in a cold part of the apparatus below the furnace. It could be raised into position by coiling the platinum wire round the extended barrel of the tap at the top of the apparatus.

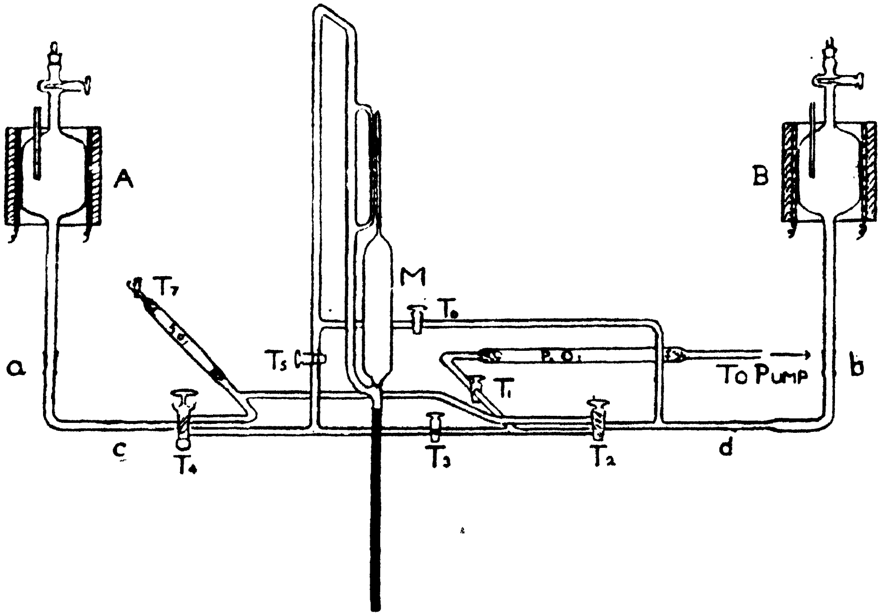

FIG. 31 (XXI³)
The apparatus of Garner and Gomm for measurement of the rate of decomposition of detonators

Procedure.—A single crystal was weighed, and its surface area determined under the microscope. It was introduced into a platinum bucket which had been previously baked out at red heat. The bucket was lowered into the reaction vessel until it was well below the furnace. The furnace was then heated to the required temperature and the apparatus evacuated overnight. (This was after the empty vessel had been previously baked out for several days.) In the morning, the furnace was lowered, and after the reaction vessel had cooled to 50°, the crystal was raised into position. Finally, the furnace was pulled up round the reaction vessel. By this method the crystal was not subjected to too rapid heating. The pumps were kept on until the temperature had reached 120°.

The crystal was heated for a short time at the highest temperature of an experiment (e.g. 280°), and then the rate of reaction was measured at that temperature until a constant rate was obtained. Subsequently, the rates were measured for lower temperatures on the same crystal. The total change in the area of interface of the crystal during a series was small, but occasionally a correction was necessary for the area of the interface.

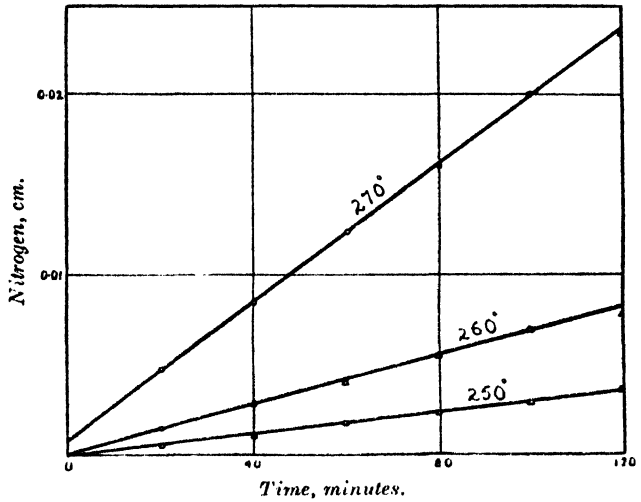

FIG. 32 (XXI[3])
Evolution of nitrogen plotted against time in the decomposition of a detonator at different temperatures

The rate of evolution of nitrogen was linear with respect to time (Fig. 32 (XXI[3])). In Table 1 are given the temperature coefficients for α-lead azide.

TABLE 1

α-LEAD AZIDE

Expt. No.	Temperature coefficient over range					
	220–30°	230–40°	240–50°	250–60°	260–70°	270–80°
15	2·04	1·67	1·94	2·33	—	—
16	—	—	—	—	3·00	2·06
18	2·05	2·37	2·25	1·93	2·31	2·93
20	2·37	2·22	2·06	1·66	2·36	4·68

The temperature coefficient is constant over the range 220–80°, and its average value is 2·43. The critical increment calculated from this is 47,600 calories, and the wave-length of the quantum corresponding with the increment is 0·5939 μ.

Sutton [1] has shown that trinitrophenylmethylnitramine gives evidence of three different mechanisms of detonation associated respectively with reaction-engines of 935, 1070, and 1160 cal./gram (water being recognized as liquid). When a pellet of an explosive of this type is enclosed in a strong container and detonated in a larger vessel in such a way that the fragments of the container and the products of decomposition of the explosive are retained within the large vessel, the energy emitted in the explosion can be measured as heat with considerable accuracy.

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[1] *Nature*, 1935, *133*, 463; *J. Faraday Soc.*, 1938, 992.

TABLE 2

Thickness of walls of container	Energy of detonation cal./gram (water liquid)
Unconfined	c. 930
$\frac{1}{64}$ in. (iron)	c. 930
$\frac{1}{16}$ in. (mild steel)	1,090
$\frac{1}{8}$ in. (,, ,,)	1,140
$\frac{1}{4}$ in. (,, ,,)	1,160
$\frac{1}{2}$ in. (,, ,,)	1,160
$\frac{1}{2}$ in. (toledo steel)	1,160

In general the quantity of energy so measured increased with increase of either (1) the strength of the container or (2) the density to which the powdered explosive has been compressed into pellets. An energy emission so variable in magnitude is not a property of the explosive alone, and one of the first problems of a practical thermo-chemist dealing with the subject consists of the discovery of conditions and limits within which an explosive can be made to detonate with a definite constant measurable emission of energy.

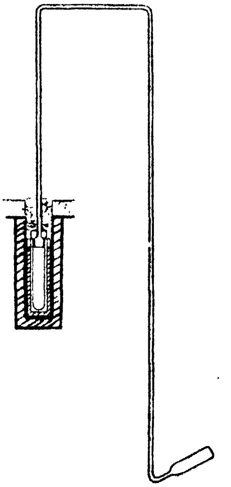

FIG. 33 (XXI³)
Farmer's apparatus for the vacuum stability test

Stability Tests. Nitric esters and related products undergo gradual decomposition on storage. Stability tests are therefore necessary as a control of the safety of explosives of this type. The tests are applied during manufacture and to the finished explosive; and they may also be applied at intervals during storage, especially in hot climates.

The usual procedure in stability tests is to subject a sample of the explosive to a raised temperature in order to increase the rapidity of the decomposition and obtain a quick indication of the stability. After heating at constant temperature for a certain length of time, the degree of decomposition is measured by one of the following methods:

(1) By indicators depending on the action of nitric peroxide
(2) Direct observation of brown fumes
(3) Measurements of spontaneous heating
(4) Methods dependng on the explosion of the sample
(5) Quantitative estimations of decomposition products
(6) Loss of weight
(7) Gasometric methods
(8) Acidity measurements

The most reliable procedure is to carry out a heating trial at a temperature not far removed from the temperature of storage, but this necessitates a prolonged trial in order to bring about a measurable degree of decomposition, and is not always practicable.[1]

For high explosives the most suitable stability test is that known as the vacuum stability test. In the Farmer test a weighed amount of the dried explosive is placed in a test-tube of the type shown in Fig. 33 (XXI[3]). The manometer is attached and the tube evacuated and placed in a thermostat. The temperature of the test varies from 80° to 180°, according to the explosive under test. The progress of the decomposition is followed by readings of a mercury manometer.

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[1] For details of these tests, *see* Reilly, *Explosives, Matches and Fireworks*, 1938.

SECTION 10: SPECTROSCOPY

(*See* Vol. II, Chap. VII, p. 289)

Emission spectra may be obtained by means of the flame, arc or spark, but it will be found for general purposes, especially when working with the ash of organic material, the arc is the most useful and most sensitive.

Arc Spectra. For this purpose a D.C. supply at 150–220 volts is desirable. A hand feed holder is used and is connected to the supply through a resistance capable of carrying 2·5–6 amperes. The electrodes of the purest carbon, copper, or iron or of the metal to be examined are fixed in the holder and the arc is struck by allowing the electrodes to touch and then separating them by 3–5 mm.

Metallic Specimens. When the specimen is in the form of a rod or is large enough to be cut into a rod, these can be used as the electrodes.

Small Metallic or other Specimens, Powders, Precipitates, &c. Pure carbon electrodes are used of which the lower one is cored and a small depression is scooped out of the core so as to leave a small cup in which the specimen is placed before the arc is struck. The lower electrode is made the positive. Electrodes of Acheson graphite, specially prepared for spectroscopic work, are very satisfactory. They are very free from iron and other impurities. Since graphite is a better conductor of heat than gas carbon, a white-hot positive crater is not formed, as is the case with ordinary carbon rods, with the result that the specimen does not vaporize so rapidly which may be an advantage when minute specimens are being examined.

Hilger copper electrodes are very pure, containing mere traces of elements other than copper. They can be used instead of carbon and here the arc is struck to heat the electrodes and is then broken while a little of the powder is added to the hot end of the lower electrode, to which it adheres.

A copper electrode can also be used to strike an arc on to a metallic object which is made the other pole: in this case no damage is done to the object other than a small arc burn. The arc is then struck and the exposure made.

Organic material should always be ashed in a silica crucible and this operation should be carried out if possible in an electric furnace at a temperature low enough to prevent the loss of metallic salts. It is important that all carbon should be removed and if there is any doubt upon this point an extract with dilute nitric acid should be made, separated, evaporated and gently ignited.

Taking Spectrograms. Two cases may be considered (*a*) when we wish to find out if a certain metal is present and (*b*) when we want to find out what metals are present. In the former case the Hartmann diaphragm is used. This is placed in front of the slit and has three holes, either of which may be opened.

First, with the bottom hole open a spectrogram of the electrodes alone is taken. Then, without altering anything else, a spectrogram of the specimen is taken with the middle hole of the diaphragm open. Finally, with the top hole open, a photo is taken of the spectrum given by the metal, in as pure a condition as possible, for which the specimen is being examined. This will be the lowest picture on the plate and when this is examined it will be a simple matter to see if the characteristic lines of the bottom spectrum are present in the middle one and absent in the top.

All the elements present in a sample may be determined with the aid of ' R.U. (*raies ultimes*) Powder '. This powder contains small quantities of fifty elements incorporated in a base material composed of the oxides of zinc, magnesium, and calcium. The quantity of each element present has been so adjusted that only the *raies ultimes* and most sensitive lines appear when the arc spectrum is obtained in the manner described. Generally about seven lines appear for each element. The method of use is to take with the Hartmann diaphragm, spectrograms of the electrodes, the specimen and then the R.U. powder. The lines present in the specimen can then be identified with the aid of a chart which identifies the lines in the powder.

High-frequency Sparks

The method described has certain disadvantages in some cases in that it generally requires the material to be reduced to the form of a powder. When organic material is present this may involve a lengthy procedure with the chance of contamination. The use of the high-frequency technique makes it possible (*a*) to dispense with this preliminary treatment and (*b*) to detect the metals present in hairs, skin, tissues, &c., without any preliminary treatment.

The high frequency is excited in an oscillating circuit which contains the secondary coil of an induction coil worked by D.C. through a make and break or which is the secondary of an A.C. transformer; across the ends of the secondary is a spark gap in which the spark is quenched by two condensers which are also in series with the primary coil of a Tesla transformer. The oscillations in the quenched spark circuit are therefore transferred by induction to the final circuit which owing to the method of coupling is traversed only by the high frequency. In this last circuit is the spark gap which is used. One electrode consists of a fine wire of gold or platinum, 0·2–0·6 mm. in diameter, which is cemented into and protected by a glass tube drawn out into a capillary and provided with the necessary means of connexion. The second electrode consists of a condenser: the dielectric is a glass plate 60 × 90 × 0·5 mm. One plate is a comparatively thick sheet of aluminium made rather smaller than the glass to prevent direct sparking and made to adhere to it with a little glycerol. The other plate is a piece of pure filter paper 30 × 60 mm. moistened with 10 per cent sodium nitrate solution. The specimen is placed on the paper. Nitrate solution is dropped on the specimen during the discharge at such a rate as to prevent the formation of a flame but not so fast as to prevent oxidation. The plate condenser is held in a movable head and is used at an angle of about 30° with the horizontal. The wire is held close to the specimen, a high-frequency discharge passes to and fro across the gap, this heats the specimen, vaporises it and renders the vapour luminous. When the spark has eaten deeply into one part of the specimen a fresh part is brought under the wire either by moving the electrode or by moving the specimen with a glass rod; in this way the focusing is not interfered with. When a sufficient part of the specimen has been treated a drop of concentrated hydrochloric acid is added to convert metals into the volatile chlorides—the spark is kept going while this is done.

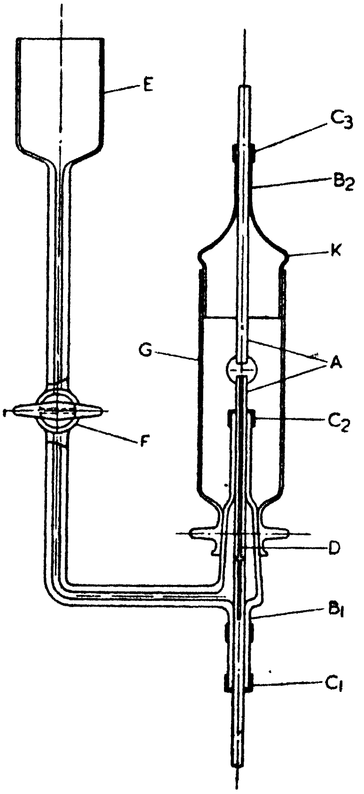

FIG. 34 (XXI^3)
Improved form of sparking tube for the spectroscopic analysis of solutions as described by Twyman, Zehden, and Dreblow

This condensed spark method gives good results in the case of slices of tissue and other material which is essentially solid, e.g. material fresh from post mortem or operation, material fixed in alcohol or formalin (here a control is done on the fixative), material embedded in paraffin (removed by zylene). Sections are cut from 0·5 to 2 mm. in thickness and are allowed to dry a little since excess of moisture increases unduly the time required for the spark to vaporize the inorganic salts.

Uncondensed Spark

This is the discharge which is obtained when the secondary of an induction coil or transformer is connected directly to the electrodes without the use of condensers or self-induction. When the induction coil is used the anode is a short thick metal rod in order to dissipate heat rapidly. The cathode is a flat platinum cup clipped to the top of a mass of iron which is cooled with ice and water in a surrounding vessel. This method is useful in the case of liquids and solutions, the cup holding about 4 ml. and being completely filled with liquid.

The Spectroscope (*see* Vol. II, p. 298)

An improved form of sparking tube for the spectrographic analysis of solutions has been described by Twyman, Zehden, and Dreblow.[1] The tube is shown in Fig. 34 (XXI^3). The spark gap is formed by two graphite electrodes A with flat ends and 5 mm. diameter. They fit well the glass tubes B_1 and B_2 and are kept in position by the rubber tubings C_1, C_2, C_3 which at the same time are liquid-tight. The solution to be analysed enters the spark through the channel D in the lower electrode. The container E is well above the spark level and has a large diameter so that during the exposure the difference in level between the spark and the surface of the liquid in the container remains practically constant. The surface of the plug of the tap F is provided with special channels which allow the tap to be set for a certain running speed without its position being very critical. In addition this gives the advantage that no narrow channels remain after the tube has been taken to pieces so that it can easily be washed out. The tube G prevents dissemination of spray. It has an aperture for the passage of ultra-violet rays. The tube B_2 containing the upper electrode is kept in position by the well-fitted lid K to which it is attached. The two rubber-covered tubes B_1 and B_2 allow the sparking tube to be fitted easily to the Hilger spark stand, contact being made by separate wires. The graphite electrodes, after having been rinsed, can be used again since, compared with the rather large quantity of solution running through during one exposure (2–4 ml.), the quantities of the previous solution which may remain after the rinsing are negligible.

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[1] *J. Soc. Chem. Ind.*, 1940, *59*, 238.

The tube gives very high intensities (especially if combined with the auxiliary series spark) and consistent sparking conditions. It has no parts liable to break down under the influence of high voltage or heat. An important condition for proper working of the tube is that reliable contacts are made between the graphite electrodes and the wires leading to them. No sparking should occur on these contacts. Good results can be obtained with crocodile clips, provided they are always kept clean and dry (especially on the lower electrode).

The Reversion Spectroscope

This instrument, described by Hartridge,[1] is particularly useful in the detection and estimation of carboxy-haemoglobin in the blood and is therefore of considerable use for medico-legal purposes.

The spectra of oxy-haemoglobin and carboxy-haemoglobin both show bands between the D and E lines but the bands of the latter are nearer the violet end of the spectrum ; the difference, however, is so slight that whatever the relative amounts of the two pigments, when both are present no more than two bands are ever seen ; there is merely an apparent shift of the bands towards the violet, always slight, but proportional to the amount of carboxy-haemoglobin present. Accurate measurement of this shift is possible by means of the reversion spectroscope which produces two exactly similar spectra, one above the other as shown on the right in Fig. 35 (XXI^3) and the upper one reversed in direction to the lower one and movable with respect to it by means of a micrometer screw. Briefly, a parallel beam of light falls on the two small angled prisms D and D′ which are fixed side by side, the one with the base up and the other with the base down, so that the beam on the left is bent slightly up and that on the right down. The beam on the left falls at an angle on the diffraction grating at G and the spectrum produced is inverted by the mirror M. The right-hand beam falls on the mirror before it reaches the grating. The mirror, which is of stainless steel, is attached to the arm which can be rotated about the fulcrum F by the micrometer screw, so moving the upper spectrum laterally. The rest of the apparatus consists of the light source L, a condenser lens C which concentrates the light on the slit S from which it passes through the glass plate micrometer GP to the achromatic collimator lens P. Two micrometer mechanisms are provided, one for coarse and one for fine adjustment. It is generally arranged so that one scale division corresponds to one Å.U.

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[1] *Proc. Roy. Soc. A.*, 1923, *102*, 575.

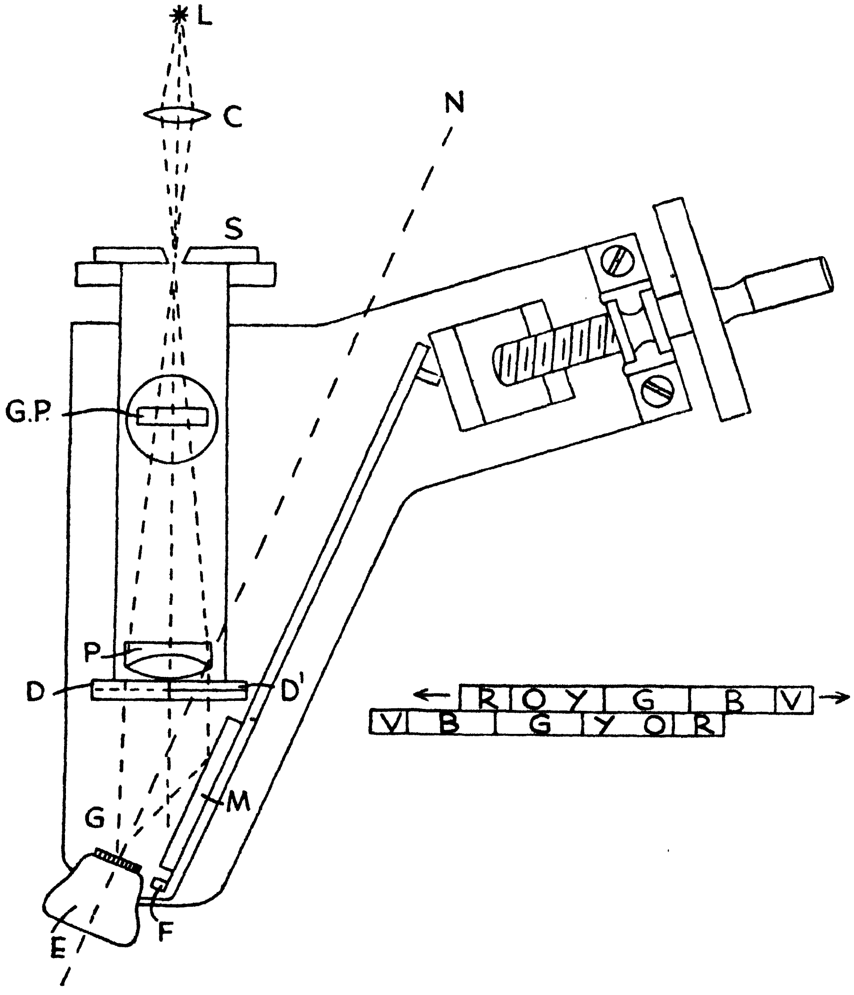

FIG. 35 (XXI^{3})
The reversion spectroscope

In using the apparatus to determine the proportions of oxy- and carboxy-haemoglobin a graph is constructed relating per cent of carboxy compound to micrometer reading in the following way:

A long rectangular glass trough divided diagonally by a glass partition is used. One compartment is filled with blood diluted to 50 times its volume with distilled water and the other with diluted blood, saturated with coal gas and with a few drops of ammonium sulphide added.

Thus with this trough placed between the slit and the light source and by the lateral movement of the trough the light may be made to traverse all relative concentrations of carboxy-haemoglobin from 0 to 100 per cent. With the trough moved to the extreme right so that only oxy-haemoglobin is present the spectra are moved so that the two narrow bands (i.e. those nearer the red) coincide and the micrometer reading is taken, several readings being made and the mean of these taken as correct. The trough is then moved, say one-tenth of its length along, so that the mixture is 90 per cent oxy- and 10 per cent carboxy-haemoglobin and the new reading taken and so on. When the results have been plotted the curve can be used for determining the percentage of haemoglobin which is combined with carbon monoxide in any sample for which the mean reading for the α band has been determined with this particular instrument. Results are said to be accurate to 1 per cent.

The Spectrocomparator was devised by P. Ellinger[1] in order to enable an estimation of a particular pigment possessing a characteristic absorption band to be carried out in the presence of other pigments, as for example in pathological urines, and also to make possible the immediate comparison of the spectra of serial eluates in chromatic absorption analysis.

The Instrument consists of a Duboscq colorimeter with a variable slit attached immediately above the top of the biprism so that the division line and the slit can be focused simultaneously by the eyepiece lens. The ordinary eyepiece of the colorimeter is replaced by a special eyepiece containing the necessary arrangement for dispersing the two beams of white light passing from the biprism and the eye lens. The illuminating apparatus and the instrument are fixed on a board or an optical bench. The illumination is provided by a 200-watt opalescent lamp at a short distance from the mirror in order to give intense illumination. The lamp-holder is adjustable in all directions in order to illuminate the mirror equally. The lamp is covered with a reflecting tin shade which is designed to prevent light from entering the observer's eye but to allow sufficient ventilation for cooling purposes. The general arrangement of the apparatus can be seen from Fig. 36 (XXI^3). Below the prism E we have the ordinary Duboscq colorimeter arrangement and then above E is the biprism F, the sharp edge of which provides the division line between the two fields. Immediately above the biprism is attached an adjustable slit G, with its opening perpendicular to the division line. If entirely opened, it does not interfere with the aperture of the absorptiometer. The top of the instrument is formed either by the usual eyepiece when the instrument is used for ordinary absorptiometric purposes, or the eyepiece is replaced by the special eyepiece shown in the figure. This consists of an eye lens H which allows simultaneous focusing of the slit and division line of the biprism. On the top of its holder rests a small angle prism *l*, the top surface of which is inclined at 45°. It provides some dispersion and straightens the beam. On its upper surface a celluloid replica of a dispersion grating J is fixed. This grating provides the actual dispersion. Above the prism *l* a ring-shaped filter-holder K is attached, and on this can rest small circular filters L. The eyepiece is terminated at the top by an oblong diaphragm M, with its length parallel

[1] *Biochem. J.*, 1942, *36*, 283.

to the division line, providing even illumination of both spectra and preventing disturbing reflections. At the level of the top surface of the prism *l* the eyepiece tube carries a side-tube. This side-tube bears on its free end an opalescent cover glass N, behind this a negative scale O, and beyond the scale a collector lens P projecting an image of the scale on the surface of the prism, which reflects this image through the diaphragm to the eye. The scale is illuminated by a 3·5 volt lamp Q fixed in a tube which can be plugged on the outside end of the side-tube.

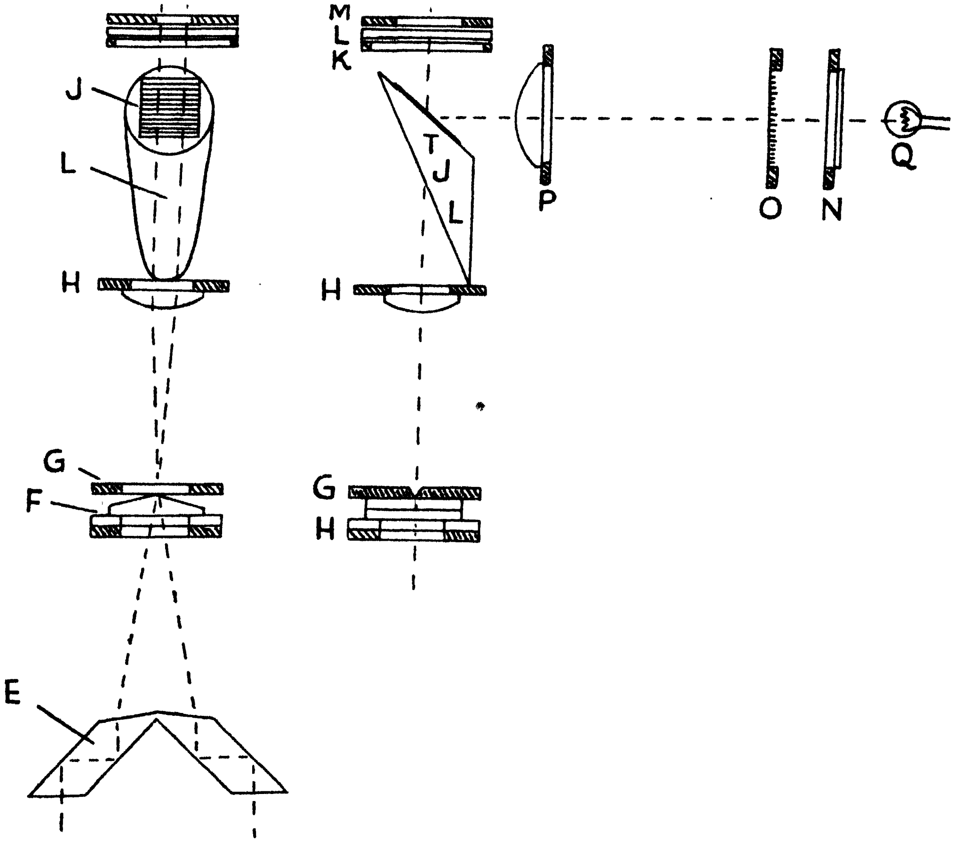

FIG. 36 (XXI[3])
The spectrocomparator of Ellinger

The two beams (indicated by dotted lines) passing through the solutions and plungers into the Duboscq prism are twice reflected into the refracting biprism where the beams are crossed. They next pass through the slit and the eye lens into the prism and the grating. Here the light is dispersed and two parallel spectra are formed, separated by an almost invisible division line. The spectra are observed through the diaphragm. By interposing filters transmitting various portions of the spectrum, small zones of the spectrum can be separated for observation. By the side of the spectrum the image of the scale appears.

Ellinger suggests several improvements for a future instrument such as inclining the eyepiece to the main tube so that the head of the observer can be placed in a more comfortable position than vertically over the instrument, dispersion to be exclusively carried out by the grating, an arrangement of a pair of wires, one above the other to avoid parallax and movable over the spectrum by a micrometer screw with a drum calibrated in wave-lengths.

Uses of the Instrument :

1. As an ordinary colorimeter or absorptiometer, by opening the whole aperture of the slit and using the ordinary eyepiece.
2. As a very bright spectroscope by using the spectral eyepiece, a narrow slit and only one of the cups. There is here the great advantage that the layer of solution can readily be varied in thickness by adjustment of the plunger.
3. For the estimation of a pigment in the presence of another pigment. This is only possible if the pigment has a band in a region where the second pigment does not absorb. In this case one cup is filled with a pure solution of known concentration of the pigment under examination and the other cup with the solution to be examined. The levels are then altered until the two bands match in intensity or better until both bands are just on the limit of visibility. Filters which transmit only in the region of the band increase the accuracy.
4. The instrument can be used for the estimation of pigments with intense absorption lines or bands if no other pigment is present in solution. In some cases, especially if the band is in the region most sensitive to the eye, i.e. between 5,200 and 6,000 Å.U., the method is considerably more sensitive than colorimetric determinations.
5. The apparatus can be used for the qualitative comparison of two spectra. This is particularly useful when examining serial eluates in chromatographic analysis because by altering the depth of the solution it is easy to see if a change in the spectrum is due only to a change in concentration or to the presence of a new pigment in the solution.

SECTION 11 : RADIOMETRIC TITRATION

Radiometric titration gives curves very similar to those obtained in Conductometric titration (*cf.* Vol. II, p. 445).

Ehrenberg [1] describes a radiometric method of titration in which an empirical standardization curve is required and considerable time is required for the establishment of radioactive equilibrium. These disadvantages are not present in the method described by Langer [2] in which radioactive phosphorus is used as the end-point indicator and the activity of the solution is measured with a Geiger-Mueller counting-tube and meter.

In reactions where a fairly insoluble phosphate is precipitated three cases are possible. In the first if a phosphate which has been rendered radioactive is titrated with an inactive solution, the radioactivity decreases as the titration proceeds and reaches a constant value which is nearly zero at the end-point so that if the activity is plotted against the volume of reagent added a curve is obtained at first sloping downwards and then becoming almost horizontal ; if the straight portions of the curves are produced, their intersection gives the end-point. The second case is the opposite of this when the liquid to be titrated is inactive and the solution added contains the radioactive phosphorus. Here the activity of the solution is very low at the start and remains so as the titration proceeds because the active phosphorus goes into the precipitate. After the end-point the added radioactive phosphorus remains in the solution so that now the activity continuously increases. In the third case where a radioactive substance is titrated with a radioactive phosphate solution or vice versa the activity decreases to a minimum at the end-point and then increases again.

Curves drawn from actual titrations are shown in Fig. 37 (XXI[3]) and illustrate the three cases. Curve *c* is an example of the first case and is for 50 ml. of 0·001 M disodium phosphate in ammonia and ammonium chloride solution titrated with 0·01 M magnesium chloride.

Curve *a* shows the reverse of this when 50 ml. of 0·01 magnesium chloride in ammonia and ammonium chloride solution is titrated with 0·1 M disodium phosphate : note the greater sharpness of the end-point with the more concentrated solutions and the resulting increase in accuracy. Curve *b* shows the titration of 50 ml. of 0·005 M uranyl acetate in ammonium acetate solution with 0·1 M disodium phosphate.

Fig. 38 (XXI[3]) shows an experimental arrangement for the realization of the method. B is the small beaker in which the titration is carried out: in it are a stirrer and the delivery tube of the 5-ml. micro-burette shown on the left. A is the thin-walled (about 0·02 mm.) Geiger-Muller counting-tube which is shielded by lead as shown by the dotted lines and is connected to the counting-meter C. The counting-tube is surrounded by a pipette which forms a concentric jacket into which the liquid from B may be drawn up through the sintered glass funnel by applying suction at the two-way tap shown on the right and from which it may be expelled and returned to the beaker by the application of pressure at the tap. The cylinder of the counter is a layer of silver chemically deposited on the inside of the glass wall and the centre wire is 3-mil tungsten. The counters were filled with alcohol (1 cm.) and argon (8 cm.). The jacket holds 5 to 10 ml. of solution. The counting-rate meter was like that described by Evans [1] and Gingrich; [2] the amplified pulses from the counter are made uniform and fed to a large condenser which leaks through a resistance and a micro-ammeter. The reading of this is proportional to the average counts per minute in the counter.

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[1] *Physikalische Methoden der analytischen Chemie*, **1936**, *1*, **383.**

[2] *J. Phys. Chem.*, **1941**, *45*, **639.**

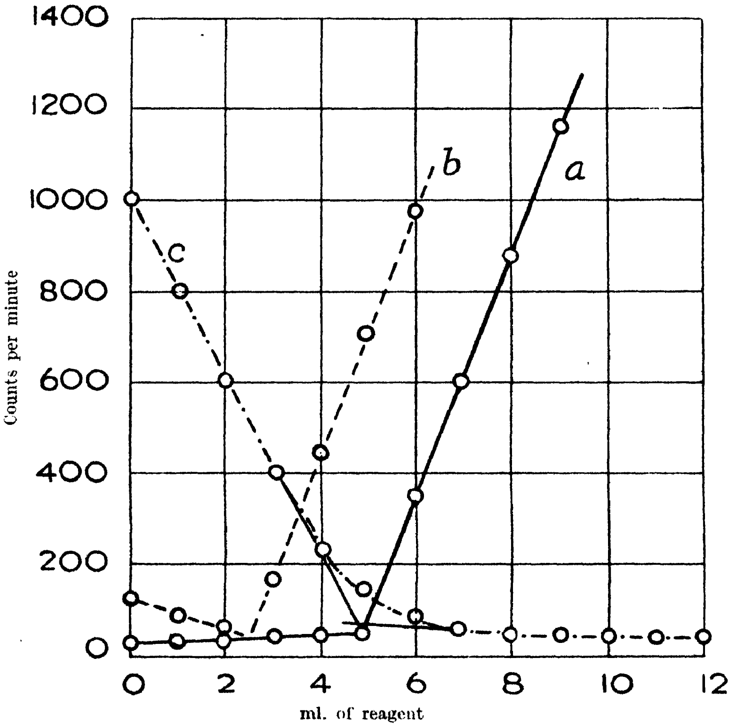

FIG. 37 (XXI[3])
Radiometric titration curves

The Indicator. Radioactive phosphorus was obtained by deuteron bombardment of red phosphorus in a cyclotron. It was oxidized to phosphoric acid and several drops of this strongly radioactive solution were added to disodium phosphate solution, so that 1 ml. of this solution when added to 50 ml. of water gave a few hundred counts per minute. This solution was then standardized gravimetrically and since the half-life period of phosphorus is 14·3 days, could be used as a reagent for several weeks; for the same reason no account need be taken of the decrease in activity during the course of a titration.

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[1] *Rev. Sci. Inst.*, 1939, *10*, 333.

[2] *Ibid.*, 1936, *1*, 450.

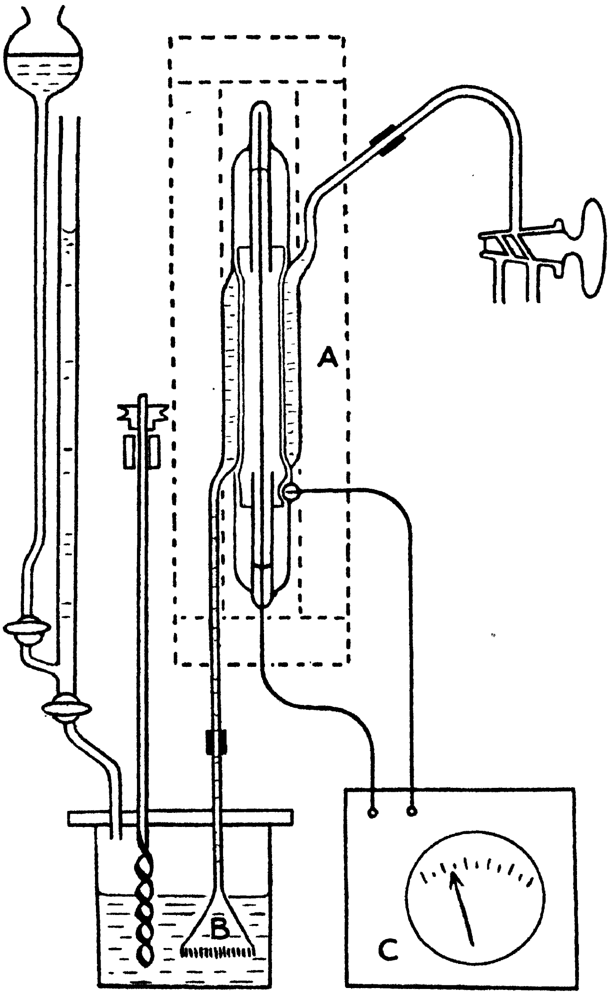

FIG 38 (XXI^{a})
Radiometric titration

Procedure. A standard solution of the substance to be determined was diluted to a known volume (25 or 50 ml.) with a solution containing chemicals to give the best condition for the reaction. The solution was sucked into the counter and the activity determined. The counter was emptied, a known volume of the reagent (0·5–1·0 ml.) was added and after thorough mixing the activity was again determined. This procedure was repeated until sufficient points had been obtained for the plot; activities were corrected for the volume change by multiplication by the factor $(V + U)/V$ where V is the original volume and U is the volume of reagent added. Titrations could be carried out with as little as 0·1 mg. of magnesium with an accuracy of about ± 2 per cent.

SECTION 12: BIOCHEMICAL APPLICATIONS[1]

In recent years there has been a wide extension of the apparatus and techniques of the physical chemist to the specialized problems of plant and animal physiology and of biochemistry generally. Some of these devices which are of broad application are outlined in this section.

Tensile Strength of Plant Sap. That powerful cohesive forces act between molecular layers in the interior of a liquid has long been recognized. Donny in 1846 found that it was possible for a column of sulphuric acid 1·255 metres long to hang in a vertical glass tube sealed at the upper end, even when the atmospheric pressure was removed from the lower end. He explained this phenomenon as due to the adhesion of the sulphuric acid to the glass and to the cohesion of the liquid itself. Berthelot a few years later succeeded in showing that water has a very considerable cohesion, and under proper conditions can sustain a great tensile stress. His method consisted of completely filling a capillary-tube with water at 28° or 30°, and sealing both ends. If the tube is then cooled to 18° the water does not contract, but still occupies the whole volume of the tube. The tensile strength of the water is thus resisting the natural contraction due to cooling.

In 1893 Böhm recorded an experiment in which a transpiring branch drew up a column of mercury above the contemporary barometric height. This experiment, in the light of our present knowledge, demonstrated clearly that the sap in the branch was in a state of tension.

Experiments made by Dixon and Joly in 1894, in which pieces cut from the wood of trees were enclosed in large sealed glass tubes without introducing weakness in the cohesion of the water, demonstrated the tensile strength up to 7 atmospheres. Further researches carried out by Dixon[2] in 1903, in which tension was applied by means of a column of mercury, showed that comparatively large pieces of living tissue, containing conducting tracts and their sap, together with parenchymatous cells, when introduced into water did not spoil its cohesive properties. These tensile properties of sap were also demonstrated up to tensions of about 150 atmospheres in capillary-tubes in later (1909) experiments.

It may be noticed that in none of these experiments was dissolved air intentionally excluded, but, rather, must have been present in the tensile liquid, owing to the procedure adopted in each experiment. In some, air-saturated water was in contact with the sap, which itself must have contained air.

A priori there appeared no reason to suspect that the tensile properties of the sap would be different from those of water. The passage of the sap through cell-walls must preclude the possibility of the entry of undissolved air, and the presence of traces of colloids in the sap could scarcely be supposed to introduce a weakness.

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[1] By Dr. Desmond Reilly.

[2] *Notes from the Botanical School, T.C.D.*, 1915, *2*, 228. *See also ibid.*, 1938, *4*, 319, and *Sci. Proc. Roy. Dubl. Soc.*, 1939, *22*, 175.

In this connexion it is worth recording that a soap film, made up with sap from the wood of *Populus* sp., even when sufficiently thin to show the ' black spot ', was found to be wonderfully stable—apparently more stable than a similar soap film made up with distilled water. This demonstrates that a film of sap not more than 12 $\mu\mu$ thick can sustain at least twice the surface tension of the soap solution, and hence sets a minor limit to its cohesion of 42 atmospheres.[1]

Dixon has found it easy to abstract sap in considerable quantities by centrifuging short lengths of decorticated stems ; and in the following he has recorded some tests on sap so obtained.

In the first instance the sap centrifuged from pieces of branches of *Fagus sylvatica*, cut from about 70 ft. above the level of the ground, was enclosed in the tension tube. This sap, after collection, was boiled on three successive days for about 1 hour in order to secure the complete wetting of dust-particles fortuitously contained in it. After its last boiling it was exposed for 24 hours as a thin layer about 4 mm. deep to the air, but shielded from dust. In this way it must have become practically saturated with dissolved air. The capillary-tube, into which it was now drawn by alternate heating and cooling, had been very carefully cleaned with a succession of chromic acid, caustic potash, and boiled water. After this cleaning the tube was boiled in water for about an hour on three successive days, heating and cooling being effected in the same water. The tube was emptied before each boiling, and allowed to fill with the freshly boiled water. The object of this was thoroughly to wet the tube and any dust particles it contained, by bringing all dissolved air on their surfaces into solution. The tube after filling with the sap to within a few millimetres of its end was sealed off. The heating of the tube was effected, as in the previous work, in a large volume of water, and was very slow.

In the first tube submitted to experiment the air-bubble disappeared at 63·50°, which may be described as the ' closing ' temperature, and reappeared with the characteristic click at 59·10°. Three other observations were made with this tube. All four agree in indicating that the sap withstood a tension of over 45 atmospheres before rupture.

A second tube was charged with some of the same sample of sap ; it was found to become completely filled at 66·25°, and ruptured at 59·50°. Calculating the tension developed in this case, the result is over 70 atmospheres. In another experiment with this tube a tension of about 50 atmospheres was produced.

It was noted by Dixon that there was no reason to believe that the tensions produced in these experiments are indications of the maximum cohesion of boiled sap. Experiments with unboiled sap in contact with vegetable conducting tracts gave breaking tensions equal to 207 atmospheres. Later experiments raised this figure to 280 atmospheres.

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[1] *Proc. Roy. Dubl. Soc.*, 109, *13*, No. 3, and *Notes from the Botanical School, T.C.D.*, 1915, *2*, 17.

Dixon measured the tensile strength of water according to the method of Berthelot. Eight capillary-tubes were used, length varying from 22 to 15 cm., and all 1·0 mm. bore. The tubes were first cleaned, a piece of yew wood introduced, and after being filled with air-free water, were kept submerged in boiling water for 1 hour or so. Before sealing the drawn-out end the water was allowed to cool and a millimetre or more of the bore was cleared of water by warming the point in the flame. The fine end was then sealed. Observations were then made of the temperatures at which the tube was full and, after slow cooling, at which rupture took place. The tension may then roughly be determined from the formula

$$B = \frac{1}{V_1} \cdot \frac{V_1 - V_2}{P_2 - P_1}$$

where B = the coefficient of compressibility of water
V_1 = Volume under lower pressure P_1
V_2 = Volume under increased pressure P_2

A tension P_2 will bring about the same change in volume in the opposite sense. The apparent change in volume of the water must be corrected for the contraction of the cooling glass. This may be allowed for by the formula

$$P = \frac{(\alpha - g)(t_2 - t_1)}{\beta\,[1 - \alpha\,(t_2 - t_1)]}$$

where P = tension
α = coefficient of expansion of water over the range
g = coefficient of cubic expansion of glass = $2{\cdot}4 \times 10^{-5}$
t_1 = temperature of rupture
t_2 = temperature when tube is full

Introducing the correction for the elastic yield of the glass, we get

$$P = \frac{(\alpha - g)(t_2 - t_1)}{\beta\,[1 - \alpha(t_2 - t_1)] + \dfrac{1}{R^2 - r^2}\left(\dfrac{r^2}{k} + \dfrac{R^2}{n}\right)}$$

where R = external radius of tube
r = internal radius of tube
k = compression modulus of glass 4×10^5 atm.
n = tension modulus of glass = 3×10^5 atm.

The constants α and β were obtained from the Landolt-Börnstein tables.

The values of P thus obtained had a least value of 37·7 atm. and a maximum value of 158·4 atm.

In making the observations the tubes were set in a large beaker of water. The temperature at which the tube became filled was first approximately determined and then, by slow heating in the correct neighbourhood, the exact determination was made. The large amount of water in the beaker ensured slow cooling, so that the temperature of reappearance of the bubble could be determined accurately.

Rosinger and Vetters[1] have determined the tensile strength of certain jellies by a method that depends on the static loading of jelly membranes. It is based on the fact that a circular elastic membrane supported rigidly at

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[1] *J. Amer. Chem. Soc.*, 1927, *49*, 2994.

the circumference and subjected to air pressure on one side takes up a spherical form. The thickness of the film is measured with a microscope by attaching a scale to an adjusting screw and focusing on the top and bottom surfaces of the membrane. The height of the spherical segment is obtained from its volume. The original should be consulted for details of apparatus and the mathematical treatment of the method. The method is applicable to the study of any elastic medium that can be formed into a membrane.

Compressibility of Liquids

A study of the compressibility—both adiabatic and isothermal—of liquids has been made by Philip,[1] using a glass piezometer. The adiabatic compressibility, specific heat at constant pressure, &c., for 24 purified liquids were determined. The isothermal compressibility and the ratio of specific heats were also obtained, in each case by calculation.

Other Botanical Techniques

A potometer method of comparing the rates of transpiration in gases supersaturated with water has been devised by Dixon and Barlee,[2] and used by them in experiments on subaqueous transpiration of plant tissues.

The convection flow in living tissues has been demonstrated by Dixon,[3] using a thermoelectric method. Such a method of measuring the velocity of flow in tubes was first used by Rein in 1929 for determining the rate of flow in blood-vessels.[4] Huber in 1932 applied the method to investigating the velocity of the transpiration current, and Dixon's method applies the use of thermocouples to the detection of the flow of materials in the bark of trees.

Dixon's method consists in essence of the local application of heat to the presumed channel of the moving liquid, and the detection of this heat with a thermocouple at a point on the channel at a measured distance from the heat source. Earlier workers had obviated the difficulty of registering also at the thermocouple heat conducted through the intervening tissues by allowing a considerable distance between heater and couple. Such distances, extending from 4 to 25 cm., were suitable where flow of velocities ranging between 5 and 30 cm. per minute were concerned. The velocities in Dixon's experiments were of the order of 1 to 2 cm. per minute or less, so shorter distances were necessary.

The error which would be caused by conducted heat, with a distance of only 1 cm. involved, was guarded against by preliminary examination of the couple. If the more-distant junction became hotter than nearer the heat source, heat by conduction through the tissues was being recorded as well as the heat by convection through the moving liquid. A momentary application of heat locally in a stem, leading to a temperature increase in the more distant junction, was therefore used to indicate a movement of material in that particular direction. The interval between the application of heat and the time in which the more distant junction became hotter than the nearer one gave a measure of the velocity of the movement. Dixon detected movement as slow as 2 cm. per hour, with thermocouples 1 cm. apart, and the near junction only 1 cm. from the heater.

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[1] *Indian Acad. Sci. Proc.*, 1939, *9A*, 109.

[2] *Sci. Proc. Roy. Dubl. Soc.*, 1940, *22*, 211.

[3] *Ibid.*, 1936, *21*, 269.

[4] *Abderhaldens Handb. der Biol. Arbeitsmethoden*, 1929, *8*, 693; and *Forschungen and Fortschritte*, 1930, *6*, 43.

The heater used was of German silver wire, 0·2 mm. diameter and 10 cm. in length. This was insulated with celluloid, folded on itself eight times, and bound tightly with silk thread. The ends were soldered to copper leads from a transformer supplying a current at 2 volts. Experiments were carried out on a horizontal branch, 2 metres from the ground, of a young ash (*Fraxinus excelsior*) about 7 metres in height. The thermocouples were of constantan and copper. Tests were carried out over a period of nearly 12 months, and 262 tests were recorded. The results established that there was mass movement both upwards and downwards, even in winter-time when the tree was devoid of leaves.

Working independently, both Renner [1] and Ursprung [2] devised a method of utilizing the mechanism supplied by the structure of the sporangium of the fern to investigate the breaking tension on fern annuli. These workers raised the breaking tension to a figure of 315 atmospheres.

OTHER APPLICATIONS

X-ray Crystallography in Biochemical Problems [3]

In recent years, extensive use has been made of X-ray methods in the examination of the states of aggregation of the molecules and submolecular units of fibres and other biochemical tissues.

The methods used for X-ray crystallographic analysis of substances of biochemical interest are essentially the same as those employed for inorganic materials, with the following exceptions :

(i) Since the spacing between molecules or sub-molecular units is the usual object of the analysis rather than the spacing between atoms, more sharply defined beams or longer wave-lengths are used ;

(ii) though there are a few instances of organic compounds in which large crystals are available and where the Laue, Bragg or oscillating crystal methods can be used, usually the materials investigated are in the form of a crystalline powder, a fibre, or a more or less random aggregate, and the Hull-Debye-Scherrer powder method or monochromatic pinhole method must be employed.

Clark [4] gives a general description of the apparatus used. Copper targets ($K_\alpha = 1{\cdot}539$ Å) are usually employed, though for very large interplanar distances, the larger characteristic radiation of iron ($K_\alpha = 1{\cdot}935$ Å), chromium ($K_\alpha = 2{\cdot}287$ Å), aluminium ($K_\alpha = 8{\cdot}31$ Å) or magnesium ($K_\alpha = 9{\cdot}86$ Å) may be used, as the spacings in the diffraction pattern are less for large interplanar distances in the specimen but greater for longer wave-lengths of radiation ($n\lambda = 2d \sin \theta$). From the results of Clark *et al.*,[5] it appears to be practicable to measure interplanar distances as great as

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[1] *Jb. wiss Bot.*, 1915, *56*, 617.

[2] *Ber. dtsch. bot. Ges.*, 1915, *33*, 140.

[3] This as well as the succeeding portions of the present section are based on the material given by Loofbourow, *Rev. Mod. Phys.*, 1940, *12*, 267–358, to whom the reader is referred for full details of results, &c. The authors wish to thank Dr. Loofbourow for assistance afforded.

[4] *Applied X-Rays*, 1940 (McGraw Hill, New York.)

[5] *J. Amer. Chem. Soc.*, 1935, *57*, 1509 ; and *Ind. Eng. Chem.*, 1931, *23*, 815.

400 Å with copper K radiation and the fibre method, if a sufficiently small pinhole (0·005 in.) and a sufficiently large specimen to film distance (20–30 cm. instead of usual 5 cm.) are used, and the central beam is carefully shielded from the plate with a small lead bead. For still larger interplanar distances they have used a magnesium target tube with camera combined in the same unit. The evaluation of large interplanar spacings from measurements of the intensity distribution in the central spot has been described by Hosemann.[1] Spacings upwards of 500 Å have been measured with copper radiation by Bernal and Fankuchen [2] with well-defined beams in work on virus proteins.

Tubes to shorten exposure times by producing high intensities of X-rays are also used. Astbury [3] employed a tube with spinning, water-cooled target to allow rapid photographing, while Clark has used a modified Ott tube in which the specimen is close to the target and the intensity correspondingly high. While filtered radiation is generally employed in the monochromatic pinhole method, Fankuchen found that spurious haloes due to the white radiation could not be sufficiently filter-eliminated in photographing the tobacco mosaic virus. He used a pentaerythritol crystal-condensing monochromator, which in conjunction with copper radiation gave high intensities and allowed sufficiently short exposure.

Infra-Red and Raman Spectra

As compounds of biochemical interest are generally complex, they are not suitable material for the infra-red analysis methods applied to simple polyatomic molecules. Besides, many such substances while water-soluble are not fat-soluble, and the high absorption of water in the near infra-red prevents their examination in dilute water solution.

The type of spectrometers used in this work are similar to those described by Coblentz.[4] They are fitted with mirrors for collimating and focusing the radiant energy beam, and with interchangeable prisms for various regions of the spectrum, ranging from quartz (1 to 3·5 μ) to KBr (12 to 22 μ). Barnes [5] has suggested certain alkali halides for infra-red prism use. Nernst glowers are the usual radiant energy sources, but Pfund [6] has devised a source using a sheet of ashed Welsbach mantle heated by an electric arc discharge and by gas. A thermopile and galvanometer may be used to measure the transmitted energy. Liquids and gases are examined in cells with windows of quartz, fluorite, &c., the transmission at each wave-length being compared with that of an optically similar cell, empty or containing solvent if the substance being examined is in solution.

Water solutions may be examined if the water absorption can be cut down to small enough figures by highly concentrated solutions. Films of tissues can be examined if held rigid over an aperture, while certain solids may be deposited as thin films on plates of KBr, rocksalt, &c. One method of wave-length calibration used is based on the prominent bands in ethyl and amyl alcohols.[7] The spectra are usually plotted in terms of percentage transmission against wave-length.

[1] *Zeits. f. Physik,* 1939, *113,* 751; *ibid.,* 1939, *114,* 133.

[2] *Nature,* 1937, *139,* 923; *ibid.,* 1937, *139,* 193.

[3] *J. Soc. Chem. Ind.,* 1930, *49,* 441.

[4] *Bull. Bur. Stand.,* 1914, *10,* 1.

[5] *J. Opt. Soc. Amer.,* 1938, *28,* 140.

[6] *Ibid.,* 1936, *26,* 439.

[7] *Ibid.,* 1938, *28,* 61.

The Raman technique has the advantage in work on biochemical compounds in that since the exciting and scattered radiation usually lie in the visible or ultra-violet regions, in which water is highly transparent, dilute water solutions can be used. Mercury-arc primary radiation, filtered to approximately monochromatic, is usually used. Spectrographs of various types may be employed, provided they have sufficient dispersion, good resolution, and sufficient speed (relative apertures ranging between *f*/3 and *f*/10). The techniques have been reviewed by Hibben and Wood.[1]

Visible and Ultra-violet Absorption Spectra

In complex biochemical molecules, the number of electronic transitions (and associated vibrational and rotational transitions) is so great that the resulting spectra may be extremely confusing. Besides, as such substances are usually examined in the liquid or solid state (or in solution), the close packing of the molecules causes perturbing influences which result in the broadening of the lines and bands into diffuse spectra. The spectral region in which the substances are examined is often one which leads to their photochemical transformation, and so gives rise to diffuse pre-dissociation or dissociation spectra. Another point is that the usual absorption techniques are not of sufficient precision and resolving power to show rotational or vibrational structure.

The results secured therefore are usually in the form of poorly defined absorption curves which exhibit one or more broad maxima and which are not generally sufficiently informative as to vibrational or rotational fine structure to permit of theoretical analysis.

Fluorescence and Emission Spectra

Applications of fluorescence spectroscopy to biochemical substances have been discussed in detail by Dhéré.[2] The principal application of emission spectra in this field to date has been in the detection of metals in tissues, and the techniques have been the standard ones with slight modifications.[3] Such techniques have also been applied in determining the metallic nutritional requirements of yeast by Richards and Troutman,[4] while Zimmer[5] has investigated the magnesium content of the blood in certain diseases by such methods.

Tissue Culture Methods

In cell-physiology research, a physical problem involved in tissue culturing concerns the use of continuous-flow devices to ensure the constant and even replacement of both the fluid medium and the atmosphere. Carrel[6] has devised a double flask connected to an external piston pump for the purpose, and Lindberg[7] has used an arrangement where incoming gas operates an aspirator flow device so dispensing with the external pump.

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[1] Hibben, *The Raman Effect and its Chemical Applications*, 1939 (Reinhold, New York); Wood, *Physical Optics*, Chap. XIV, 1934 (Macmillan).

[2] *La Fluorescence en Biochemie*, 1937 (Les Presses Universitaires de France, Paris).

[3] *Vide* Gerlach and Gerlach, *Clinical and Pathological Applications of Emission Spectra*, 1934 (Adam Hilger, London).

[4] *J. Ind. Hyg. Toxicol.*, 1939, *21*, 446.

[5] *Spectrochem. Acta L*, 1939, 93.

[6] *Comptes Rendus Soc. Biol.*, 1931, *7*, 106.

[7] *J. Exp. Med.*, 1935, *62*, 409; and Carrel and Lindberg, *The Culture of Organs*, 1938 (New York).

Lindberg has also developed continuous-flow perfusion equipment by which whole organisms may be cultured.

In measuring the growth of cultures, the usual method of determining the surface area at various stages of growth is far from providing a satisfactory index. Though optical transmittancy measurements have had little success so far, it is now believed that an improved optical method, using monochromatic ultra-violet light near 2,600 Å, highly absorbed by nuclear material, may lead to a practical method of accurately assessing growth.

Measurements of cellular respiration and glycolysis can be carried out by micromanometric methods, and the same type of equipment may be used for studying chemical reactions involving small amounts of gas exchange.

The techniques used in the study of cell metabolism have been described by M. Dixon and by Fenn.[1] Linderstrøm-Lang [2] has applied the cartesian diver principle to the contruction of very sensitive manometers which can measure quantities of absorbed or evolved gas as small as 0·002 ml. When readings are to be taken, the diver is brought to a fixed mark on the vessel by a known external pressure. Modifications of this method have been described by Needham *et al.*,[3] while several respirometers have been devised for measuring the oxygen consumption of small animals.

In studies of intercellular physiology, recent use has been made of physical agents instead of chemical agents to affect cell activity. Such agents include lethal ultra-violet light and mechanical vibrations.[4] These physical agents have the advantage over chemical factors that a careful control of conditions is possible, and the difficulty of the carrying over of the original agent in the cell-free liquid is of course obviated. The applications of such techniques are still only in their early stages.

[1] *Vide* M. Dixon, *Manometric Methods*, 1934 (Camb. Univ. Press, Cambridge); and Fenn, *The Differential Volumeter for the Measurement of Cell Respiration and Other Processes*, 1935 (Amer. Instrument Co., New York).

[2] *Nature*, 1937, *140*, 108.

[3] *Proc. Soc. Exp. Biol. Med.*, 1938, *39*, 287.

[4] *Vide Bull. Bas. Sci. Res.*, 1933, *5*, 13 ; *ibid.*, 1933, *5*, 33 ; *Nature*, 1934, 133, 909 ; *ibid.*, 1937, *139*, 539 ; *ibid.*, 1937, *140*, 611 ; *ibid.*, 1939, *144*, 553.

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„ 2. *ibid.*, 1944, *15*, 575.
„ 3. *ibid.*, 1945, *16*, 373.

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